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CRYSTAL-OPTICAL METHOD FOR DETERMINING THE STRUCTURES OF COMPLEX COMPOUNDS

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In recent years, in the Department of Crystallography and Crystal Chemistry of the Moscow State University and in the Crystal Chemistry Laboratory of the Institute of General and Inorganic Chemistry of the Academy of Sciences of the USSR, a new crystal-optical method has been developed for determining the structures of complex compounds [1, 2, 3]. By this method the geometric configuration, and sometimes also the interatomic distances in the inner sphere of the complex compound, can be determined with adequate accuracy.

The determination of the geometric configuration is based essentially on a comparison of the experimentally measured refractive indices with the theoretically calculated values (from the component refractions) for the various isomeric forms. The refractive indices are calculated from the Lorentz-Lorenz formula, which is solved for n^2. Hence, for the calculation of the refractive indices of complex compounds, the component refractions must be known.

The molar refractions of ionic compounds in the crystalline state can, to a first approximation, be compounded additively from the ionic "crystal" refractions, as we have shown in previous papers [1, 3]. Hence, for the calculation of the refractions of ionic complex compounds, it is sufficient to know the refractions of the corresponding ions.

The refractions of cations have been determined by Fajans [4] for the gaseous state. Since variations in the refractions of cations due to changes in polarization conditions can be neglected, Fajan's values can be used directly for the calculation of the molar refractions of solid salts, including salts having complex anions. The refractions of simple anions are given for the crystalline state in our previous papers, cited above, where they were determined from data for crystals of alkali-metal salts. The refractions of complex ions can be calculated from coordinate refractions [5]; thus the refraction of the ion $[PtX_4]$ is three times that of the $X-Pt-X$ coordinate, the refraction of the ion $[PtX_5Y]$ is the sum of two $X-P-X$ refractions and one $X-Pt-Y$ refraction, and so on. The coordinate refractions for bi- and quadri-valent platinum and tervalent cobalt compounds have already been published by us [6], and the experimental data from which the coordinate refractions of quadrivalent platinum were calculated are given in the present paper. It must be pointed out that the Lorentz-Lorenz formula by which the refractions were calculated is strictly applicable only to isotropic media and to refractive indices extrapolated to infinite wavelength. Since the crystals of almost all of the compounds considered in this paper are optically anisotropic, the value of refractive index that we have substituted in the formula is averaged by the formula $n = \frac{1}{3}(n_g + n_m + n_p)$ and is extrapolated to infinite wavelength with the aid of the dispersion measurements.

The present paper is concerned with the determination of the geometric configuration of complex compounds of quadrivalent platinum. We have measured the dispersion of the refractive indices for several quadrivalent platinum complex compounds and calculated the refractive indices for infinite wavelength. The densities of most of the compounds were measured in M. M. Yakshin's laboratory, and we determined some of them ourselves by means of a pyknometer.

Table 1 gives the data on the dispersion of the refractive indices of quadrivalent platinum compounds. The extrapolation was carried out graphically by Wulf's method [7].

From the experimental data we calculated the coordinate refractions for quadrivalent platinum compounds. In these calculations we used our previously published ionic refractions [3] and the refraction for crystallization water as determined by Batsanov [8]. In the calculation of the refraction of the coordinate $NH_3-Pt-NO_2$ from the data for dichlorodinitroammineplatinum, account was taken of the formation of a hydrogen bond $NH\ldots O$ (between oxygen of the nitro group and hydrogen of ammonia) by making the necessary correction (0.38 cc) [8].

From the data in Table 2 the geometric configurations of a group of chloroammine and chloronitro quadrivalent platinum compounds can be determined. Results of these calculations are given in Table 3.

It will be seen from Table 3 that the square of the refractive index calculated for the actual structure of the

TABLE 1

Formula of compound	λ	486	520	555	589	620	656	∞
$(NH_4)_2PtCl_6$	n_m	1,878	1,863	1,853	1,843	1,836	1,830	1,713
$Pt(NH_3)_2Cl_4$ cis	n_g	2,040	2,020	2,006	1,994	1,985	1,977	1,820
	n_m	1,909	1,893	1,882	1,870	1,863	1,855	1,716
	n_p	1,877	1,862	1,852	1,842	1,835	1,829	1,712
$Pt(NH_3)_2Cl_4$ trans	n_g	2,047	2,027	2,013	2,002	1,992	1,984	1,826
	n_m	1,889	1,878	1,867	1,856	1,849	1,843	1,717
$[Pt(NH_3)_3Cl \cdot H_2O$ trans	n_g	1,909	1,893	1,882	1,870	1,863	1,855	1,716
	n_m	1,806	1,792	1,782	1,772	1,766	1,761	1,654
	n_p	1,720	1,709	1,701	1,694	1,689	1,684	1,593
$[Pt(NH_3)_4Cl_2]\ Cl_2$ trans	n_g	2,042	2,022	2,008	1,996	1,987	1,979	1,821
	n_m	1,773	1,761	1,753	1,745	1,739	1,735	1,635
$Pt(NH_3NO_2)_2Cl_2$	n_m	1,815	1,803	1,793	1,784	1,777	1,771	1,655
$K_2Pt(NO_2)_2Cl_3$ cis	n_g	1,918	1,902	1,891	1,879	1,872	1,864	1,728
	n_m	1,822	1,809	1,800	1,791	1,784	1,779	1,666
	n_p	1,768	1,756	1,748	1,740	1,734	1,729	1,628
$K_2Pt(NO_2)_2Cl_3$ trans	n_g	1,822	1,809	1,800	1,791	1,784	1,779	1,666
	n_m	1,792	1,778	1,769	1,761	1,755	1,750	1,645
	n_p	1,749	1,737	1,728	1,720	1,715	1,711	1,609
$K_2Pt(NO_2)_4Cl_2$ cis	n_g	1,844	1,830	1,820	1,210	1,803	1,797	1,676
	n_m	1,787	1,773	1,764	1,756	1,750	1,745	1,640
	n_p	1,753	1,741	1,732	1,724	1,719	1,715	1,613
$K_2Pt(NO_2)_4Cl_2$ trans	n_g	1,813	1,800	1,790	1,780	1,774	1,769	1,651
	n_m	1,757	1,746	1,738	1,730	$1,724_5$	1,720	1,618
	n_p	1,741	1,731	1,723	1,716	1,711	1,706	1,614

TABLE 2

Coordinate	Compound	M	d	π_∞	$R^\infty_{com\text{-}d}$	R^∞_{coord}	
Cl – Pt – Cl	K_2PtCl_6	486,16	3,474	$1,722_5$	55,42	16,97	16,90
	$(NH_4)_2PtCl_6$	444,05	3,065	1,713	56,79	16,84	
Cl – Pt – NH_3	$Pt(NH_3)_2PtCl_6$ cis	371,06	3,420	1,750	44,20	13,65	
NH_3 – Pt – NH_3	$[Pt(NH_3)_4Cl_2]Cl_2$ trans	405,18	2,927	1,695	53,21	9,83	
NH_3 – Pt – NO_2	$Pt(NH_3NO_2)_2Cl_2$	392,14	3,040	1,655	45,86	14,29	
NO_2 – Pt – NO_2	$K_2Pt(NO_2)_4Cl_2$ trans	528,37	3,140*	1,628	59,72	19,16	
NO_2 – Pt – Cl	$K_2Pt(NO_2)_4Cl_2$ cis	528,37	3,156*	1,643	60,54	18,44	18,50
	$K_2Pt(NO_2)_3Cl_3$ cis	517,82	3,226	1,673	60,17	18,56	

*Measured by us.

TABLE 3

Formula of compound	M	d	$\bar{n}^2_{opt}$	R_∞	$\bar{n}^2_{calc}$	Δn^2_∞
$Pt(NH_3)_2Cl_4$ trans	371.08	3.508	3.071	cis 44.16 trans 43.63	3.150 3.106	0.079 0.035
$[Pt(NH_3)_4Cl_2]Cl_2$ trans	405.18	2.927	2.871	cis 53.71 trans 53.19	2.902 2.872	0.031 0.001
$[Pt(NH_3)_3Cl_3]Cl \cdot H_2O$ trans	406.16	2.877	2.741	cis 52.24 trans 51.98	2.762 2.748	0.021 0.007
$K_2Pt(NO_2)_2Cl_2$ cis	517.82	3.226	2.799	cis 59.82 trans 59.06	2.785 2.746	0.014 0.053
$K_2Pt(NO_2)_2Cl_2$ trans	517.82	3.151	2.689	cis 60.00 trans 59.06	2.725 2.683	0.036 0.006
$K_2Pt(NO_2)_4Cl_2$ trans	528.37	3.156	2.699	cis 60.78 trans 59.72	2.710 2.663	0.011 0.036

compound is always much closer to the experimental value than the value calculated for the isomeric structure. It follows that the geometric configurations of complex compounds of quadrivalent platinum can be determined by comparing the calculated and experimentally measured refractive indices.

The last compound listed in Table 3 was synthesized recently in A. V. Babaeva's laboratory, and the crystal-optical method has provided the first physicochemical proof of the structure of this interesting complex compound.

In conclusion we will point out the advantages of the crystal-optical method: first, there is the rapidity with which questions of structure can be resolved (the whole of the work can be done in 1-2 days); and second, there is the lack of stringent requirements with respect to the quality of the sample investigated (very small, poorly formed crystals, and also amorphous powders, can be investigated by this method).

These advantages of the refractometric method, coupled with its general suitability for the resolution of questions of structure, give us reason to hope that it will ultimately become one of the working methods of the chemistry of complex compounds. The refractometric method can be applied also in the solution of theoretical problems: thus it enables an approach to be made to the quantitative evaluation of the trans effect [6].

SUMMARY

The crystal-optical method for determining the structures of complex compounds has been extended to compounds of quadrivalent platinum. The structure has been determined, for the first time, of a compound, $K_2Pt(NO_2)_4Cl_2$, recently synthesized by A. V. Babaeva; it has been shown to be the cis isomer.

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STRUCTURE OF SODIUM BOROSILICATE GLASSES IN ITS RELATION TO THE PHENOMENON OF OPALESCENCE

COMMUNICATION 2. INVESTIGATION OF THE STRUCTURE OF POROUS GLASSES*

S. P. Zhdanov, E. A. Porai-Koshits, and D. I. Levin

By the treatment of sodium borosilicate glasses of certain compositions with various acids it is possible to prepare porous glasses, the structures of which (the sizes and forms of the pores and the internal surface area) depend on the composition of the original glass, the thermal history of the glass, the concentration of the acid, the brittleness of the pieces of glass being treated, the temperature of the treatment, and so on [2, 3]. The object of the investigation described in this paper was the establishment of the relationship between the structure of a porous glass and its opalescence. The method of preparing the samples and the leaching conditions were therefore standardized as far as possible, and only the thermal treatment of the original glass was varied, this being responsible for the degree of opalescence (which was varied down to a state of complete clarity) of a glass of given composition.

EXPERIMENTAL

The structures of the porous glasses were studied by three independent methods: the adsorption method, the method based on the low-angle scattering of X-rays, and the electron-microscope method. Since the problem of investigating the structures of highly dispersed substances is very complex, the simultaneous application of several methods, each of which has specific merits and demerits, should ensure that the conclusions based on the investigation will be reliable.

1. Adsorption Method

The adsorption method for the investigation of the structures of porous substances is simple and has been used extensively [4-6]. Adsorption and desorption isotherms provide the basis for the determination of the main elements of the structures of porous adsorbents, i.e. the total volume of the pores, their surface area, and their effective radii.

The first investigations of one of the authors [3] showed that the structures of porous glasses in the state in which they are obtained after the acid treatment, as determined from vapor-adsorption isotherms, are usually independent of the opalescence properties of the original glasses. Further investigations have shown, however, that it is possible, under certain conditions, to find considerable differences in structure between porous glasses prepared from opalescent and nonopalescent glasses. These differences are observed when the porous glasses are treated with alkali, and they are found to be related to the structures of the original sodium borosilicate glasses [7]. Our previous investigations were carried out on a glass of composition Na 70 – 23**. In this section of the paper we are concerned with the glasses Na 75 – 20, Na 65 – 28, and Na 65 – 30.

By holding the glasses at temperatures of 650° and 725°, we obtained opalescent and nonopalescent samples, respectively. The porous glasses were prepared by treatment of glass powder in 3 N HCl at 50°.*** For all of the samples of porous glass, the isotherms for the adsorption and desorption of methanol vapor at 15° were determined before and after treatment of the glass with 0.5 N KOH for one hour. Typical isotherms for samples prepared from

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* The first communication described an investigation by the authors of the opalescence of sodium borosilicate glasses [1].

** The first figure denotes the mole percentage of silica and the second that of boric anhydride; the remainder is sodium oxide.

*** To denote porous glasses obtained from glasses of various compositions quenched from different temperatures we shall write expressions such as $[Na\ 70-23]_{725°}$, in which the subscript is the temperature from which the original glass was quenched.

opalescent and nonopalescent glasses are given in Figs. 1 and 2.

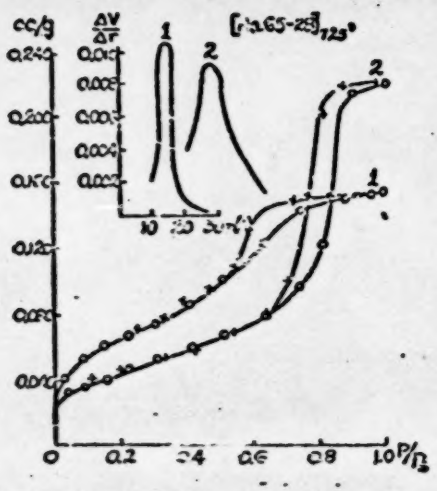

Fig. 1. Methanol adsorption isotherms before (Curve 1) and after (Curve 2) treatment of the glass with alkali.

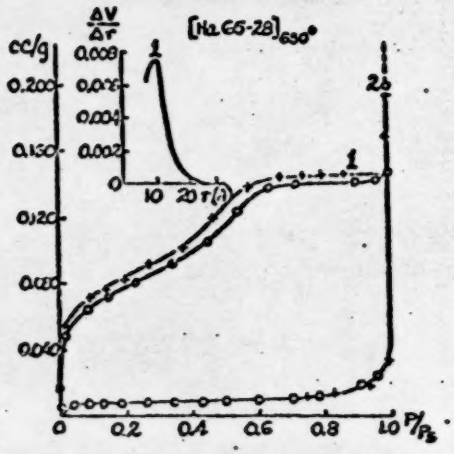

Fig. 2. Methanol adsorption isotherms before (Curve 1) and after (Curve 2) treatment of the glass with alkali.

Table 1 gives values, calculated from the isotherms, for the total volume of pores, their surface, and their most probable radius for all of the glasses investigated, before and after the alkali treatment.

From Figs. 1 and 2 and Table 1 it can be seen that treatment of porous glasses with 0.5 N KOH always increases the total volume of pores and their radii, but results in a reduction in adsorptive power at low relative pressures, and therefore in a reduction in surface area. It will be immediately obvious that porous glasses prepared from opalescent and nonopalescent glasses of the same composition yield products differing greatly in properties and in structure.

TABLE 1

Composition of original glass	State of original glass	Before alkali treatment			After alkali treatment		
		total volume of pores (cm^3/g)	surface area (sq. m/g)	predominant pore radius (A)	total volume of pores (cm^3/g)	surface area (sq. m/g)	predominant pore radius (A)
NA 75 – 29	Nonopalescent	0.143	260	13	0.166	228	20
	Opalescent	0.109	213	10	0.348*	38	~300
Na 65 – 28	Nonopalescent	0.153	198	15	0.220	140	28
	Opalescent	0.146	232	11	0.200*	26	~300
Na 65 – 30	Nonopalescent	0.247	300	18	0.364	246	28
	Opalescent	0.244	280	34	0.458*	212	~300

* Equilibrium at $p/p_s = 1$ was established very slowly, and it is possible that in these experiments the limiting value of the sorption was not attained in 24 hours.

In the first case treatment of the porous glasses with alkali yields very coarsely porous products and results in a considerable reduction in surface area* . For these products capillary condensation begins only when p/p_s

*The glass [Na 65 – 30] is exceptional. It is clear that when this glass is treated with alkali the formation of the very large pores characteristic of all opalescent glasses does not prevent the retention of a considerable number of fine pores.

is close to unity, and there is no second inflexion in the curve in the region of capillary condensation. When the glass powder is washed with water after the alkali treatment, the alkali is readily removed from within the grains of the powder, and already after 2-3 hours no trace of alkali can be detected with phenolphthalein. In the second case the pore radii of porous glasses are not significantly increased and the surface area is only slightly reduced. There is a second point of inflexion on the isotherms, and the region of capillary condensation is limited by certain upper values of p/p_s that are less than unity. Alkali is removed only very slowly when the glass powder is washed with water – several days are required. It must be emphasized that, before the alkali treatment, the porous glasses that are being compared were extremely similar in properties and structure (see the 3rd, 4th and 5th columns of Table 1).

It is very difficult to interpret the results if it is assumed that the increase in the radii and total volume of the pores occuring when porous glasses are treated with alkali results from the gradual widening of the pores by the dissolution of the silica forming their walls and that the rigid skeleton of a porous glass is formed throughout by silica of constant characteristics through which the pores are distributed uniformly. The following objections can be raised to these ideas: 1) if the pores are constantly becoming wider as the silica forming their walls dissolves, their surface area should increase, and not diminish, which is what it actually does; 2) the volume of the pores does not increase in proportion to the square of the radius, but at a much lower rate; 3) no explanation is provided for the great difference between opalescent and nonopalescent glasses with respect to the solubility of the silica of the pore walls; 4) the thickness of the walls of the pores of porous glasses cannot be so great that an increase in pore radius under the action of alkali from 10 to 300 A would not result in the total destruction of the porous structure.

The experimental results are satisfactorily explained if it is assumed that porous glasses can be represented as a combination of two structures: the coarse structure of the silica skeleton, i.e. that part of the structure of the original glass which was formed mainly of silica and remained almost unchanged during the treatment with acid; and the fine secondary structure within the cells of the skeleton [3]. This secondary structure is built of finely dispersed, hydrated silicic acid; it was formed during the interaction of the sodium borosilicate glass with acid [1]. It is logical to assume that the rate of dissolution of the finely dispersed silicic acid in alkali will be much greater than that of the vitreous silica of the walls of the coarsely built skeleton. The fine structure of the pores may be completely destroyed in a short treatment with 0.5 N KOH in the cold, whereas the structure of the coarsely cellular skeleton will suffer no appreciable change during the same time. When alkali-treated porous glasses are washed with water, the reaction products that have accumulated within the cells of the skeleton will be extracted, and the resulting porous product will retain all the peculiar features attributable to the silica skeleton.

According to this view of the structure of porous glasses and the mechanism of the action of alkali, the destruction of the fine structure will be accompanied by a great increase in the radii of the pores and a reduction in pore surface as the total volume of pores increases, and this is the phenomenon that is actually observed. Hence, treatment of porous glasses with alkali lays bare the silica skeleton, which is masked in porous glasses by a fine secondary structure, and makes it accessible for investigation by adsorption methods. It is evident that this fine structure is not in any way related to the opalescence of the original glass, but the structure of the silica skeleton is closely related to the opalescence characteristics of the sodium borosilicate glass, as the results described above and previously [3, 7] show.

2. Method based on the low-angle scattering of X-rays

Investigation by the low-angle scattering of X-rays permits the detection of regions of inhomogeneity in the material under examination which have linear dimensions of 20 to 1000 A and higher. The theory of the method, the experimental technique, and the first attempts to apply it to porous glasses have already been described [8-10]. It has been established from observations on the effect of artificially widening the pores that low-angle scattering by porous glasses is almost always determined by the pores, the radii of which can be determined by analysis of the diffraction pictures [11].

In order to investigate the effect of the thermal treatment of the original sodium borosilicate glasses on the structures of the porous materials obtained from them by the action of acids, glasses of six different compositions were examined: Na 75 – 20, Na 70 – 24, Na 70 – 23; Na 65 – 30, Na 65 – 28; and Na 60 – 30. Two samples of each of these were heated for two hours at different temperatures, differing by 5-20° and chosen so that, as far as possible, the maximum opalescence would be obtained at the lower temperature, and complete clarity at the higher. The values of these temperatures, which were measured accurately within ± 3°, depended on the composition and previous thermal history of the glass. After being heated, all of the glasses were ground and treated with 3 N HCl under standard conditions. The X-ray diagram was obtained in the apparatus already described [10]*.

* The preparation and X-ray investigation of the specimens were carried out by the graduate student N. G. Minaev.

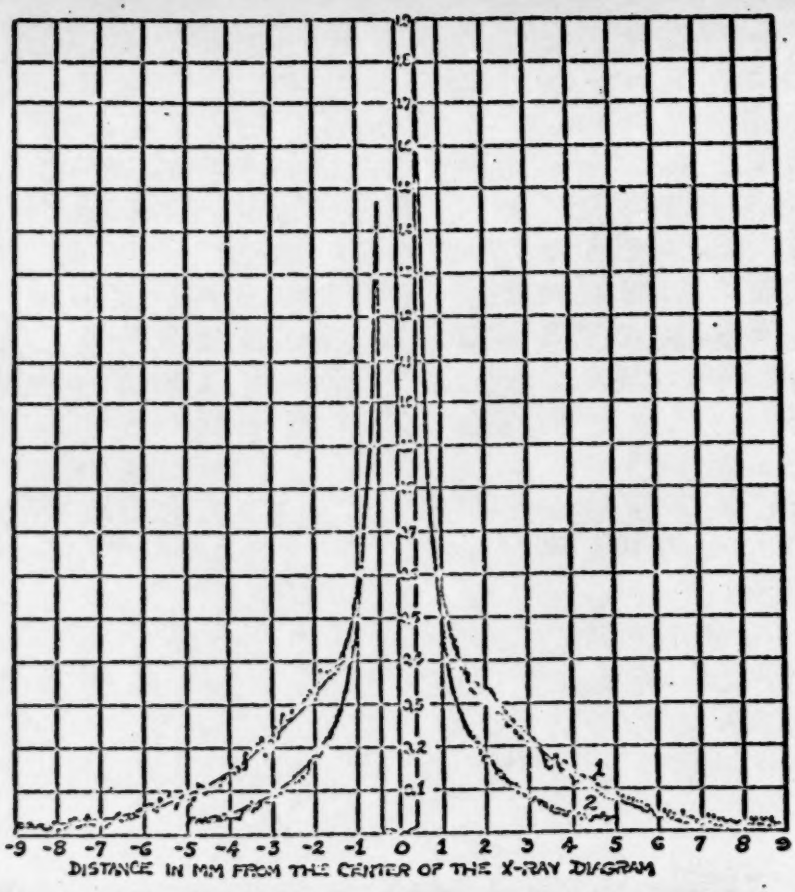

Fig. 3. Microphotometric curves for the porous glass [Na 70 −23]$_{705°}$, before (1) and after (2) its treatment with 0.5 N KOH

Fig. 3 shows the microphotometric curves for the porous glass [Na 70 −23]$_{705°}$, before and after the alkali treatment. These results differ from those of the adsorption investigation in that the coarsely porous structure — which is responsible for the intense scattering at the very lowest angles (the coincident parts of the curves) — is revealed by the X-rays not only after, but also before the alkali treatment of the porous specimen. The two curves differ only at the highest angles, i.e. in the part concerned with scattering by the highly dispersed secondary structure. Also, the removal of this highly dispersed part increases the total scattering intensity, as determined from the exposure, sometimes twenty or thirty times. This indicates a great increase in the difference between the electron densities of the walls of the basic silica skeleton and those of the channels freed from secondary silicic acid. This result provides convincing confirmation of the results of adsorption investigations [3], and it enables us to utilize the effect of alkali for the purpose of shortening the exposure, since it is the structure of the basic skeleton, not that of the secondary silicic acid, which is of interest to us in the present investigation. For this reason, before being examined by X-rays, all of the glasses were treated with alkali, washed, and dried.

The microphotometric curves for all of the samples provide an extremely clear illustration of the main result of the X-ray investigation: as the opalescence of the original glass disappears (i.e. as the temperature of treatment rises), the structure of the porous skeleton of the porous glass undergoes great changes, the large channels or cells (original glass opalescent) being replaced by finer channels (original glass clear). This can be seen, for example, when the microphotometric curves for the porous glasses [Na 70 −23]$_{700°}$ and [Na 70 −23]$_{705°}$ are compared (Fig. 4).

The sharp fall in the scattering curve for very low angles (about 10') indicates the coarsely porous structure

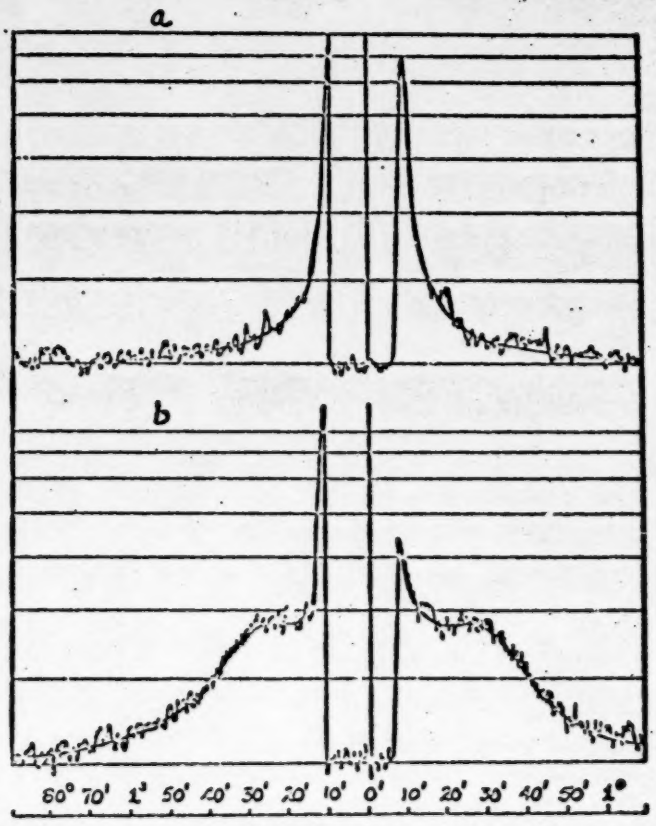

Fig. 4. Microphotometric curves for porous glasses: a) [Na 70 −23]$_{750°}$; b) [Na 70 −23]$_{750°}$

of the glass, the pores of which do not form a closely packed system; and the slower fall in this curve at angles of about 1.5° is concerned with the finely porous structure of the glass, and the presence of inflexions, or of a maximum (clearly manifest after the introduction of the collimation correction) points to fairly close packing of these pores. We may point out that this close packing is confirmed by electron micrographs (see Fig. 8), in which the walls between the fine pores are seen to be very thin.

Some of the microphotometric curves give clear indications of the presence of a dual structure in the specimens; this may be explained by inadequate thermal treatment of the original glasses, the disappearance of the opalescence and the structure associated with it being then incomplete. Other features of the curves are the rapid fall at the very lowest angles (associated with coarse pores) and "wings" (associated with fine pores). The correctness of the explanation is readily proved by a simple summation of the ordinates of the scattering curve for two extreme cases – for glass without fine pores, and for glass without coarse pores – as shown in Fig. 5 for the glass [Na 70 −23] prepared from an original glass that had been cooled slowly. The summation curve (broken line) is almost coincident, within the experimental error, with the curve for the porous glass [Na 70 −23]$_{750°}$, thus showing that both structures are present in this glass.

The above discussion is illustrated in the scheme in Fig. 6, in which intensity curves of various types are given. Quantitative calculations by different methods are possible for two types of curves – those for samples containing only large pores, and those for samples containing only fine pores, i.e. samples prepared from glasses that are opalescent throughout and those prepared from glasses that are completely clear throughout, respectively.

Curves of the first type, which have no maxima or points of inflexion, can be replaced by an exponential function, or a sum of exponentials, and so do not require a collimation correction in the determination of pore radii by the "method of tangents" [3]; the collimation correction would not affect the form of the ($\log I$, ϑ^2).

graph from which the radii are determined (I is the intensity and φ is the scattering angle).

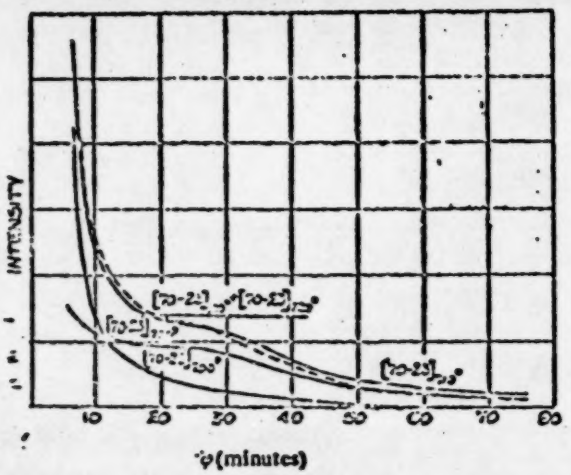

Fig. 5. Summation of the intensity curves for the crucible glasses [Na 70 − 23]$_{70°}$ and [Na 70 − 23]$_{28°}$, indicating the presence of dual structure in the glass [Na 70 − 23]$_{28°}$.

The results of calculations on such curves indicate not only that the main skeletons of samples obtained from opalescent glasses have a coarsely porous structure, but also that they have a polydisperse character; it is in fact generally impossible to determine the upper limit of the pore or channel radii, since the relevant part of the scattering curve lies at very low scattering angles, which cannot be examined with the apparatus at our disposal (less than 6'). For this reason, the mean pore dimensions that we shall cite for samples of this type must be regarded as somewhat low.

Curves of the second type, which are given when the original glasses are completely clear, always have "wings", i.e. maxima and inflections at fairly high scattering angles; they may even consist solely of such "wings". For such curves a collimation correction was introduced, and as a result a corrected curve was obtained for ideal experimental conditions – a primary X-ray beam of zero section incident on the specimen. The interference maximum became sharper and moved to higher scattering angles, and the form of the curve altered to some extent.

This was mainly an indication that the pores were fairly closely arrayed. The mean pore radius was determined from the new position of the maximum from the formula [11]:

$$R \approx 0.32 \frac{\lambda}{\varphi_{max}}$$

(λ is the wavelength of the rays used, and φ_{max} is the scattering angle at the intensity maximum.)

The values of pore radii calculated in this way were compared with those determined by the first method (method of tangents) as applied to the "tail" of the curve, i.e. the part of the curve corresponding to the highest angles (the interference maximum, while greatly affecting the central part of the curve, has little effect on its beginning and terminal parts; the method of tangents cannot, however, be applied to the beginning part of the curve, i.e., at the lowest angles, owing to the experimental inaccessibility of this part).

For all of the finely porous samples, excellent agreement was obtained between the two methods of calculation. Strictly speaking, this proves only that it is the pores of smallest radius that are closely packed, resulting in the appearance of an interference maximum. However, the absence of any appreciable scattering at the very lowest angles enables us to infer that there are no pores of greater radius in the samples, at least in the range of dimensions in which we are interested. It may be concluded, therefore, that the finely porous samples obtained from clear glasses are monodisperse.

Table 2 gives the results of the calculations for all of the investigated samples. It will be seen from these that the mean radius of the main channels of samples obtained from opalescent glasses is several times, some times more than ten times, as great as the mean radius of the main channels of samples prepared from clear glasses.

It is interesting to note that it is the glasses that were not obtained in a completely clear state (Na 70 − 24, Na 65 − 30 and Na 65 − 28) which have given products, after treatment with acid and alkali, having pores of large radius (61, 59 and 79 A respectively), as compared with those of the remaining samples. This can be ascribed to the effect of the opalescent part of the original samples. It may therefore be assumed that radii of 35-45 A are characteristic of the main channels in all porous glasses obtained from glasses that have been heat-treated at temperatures above those of the opalescence zone, i.e. that the dimensions of the regions of inhomogeneity in clear glasses of this sort are not greatly dependent on their composition.

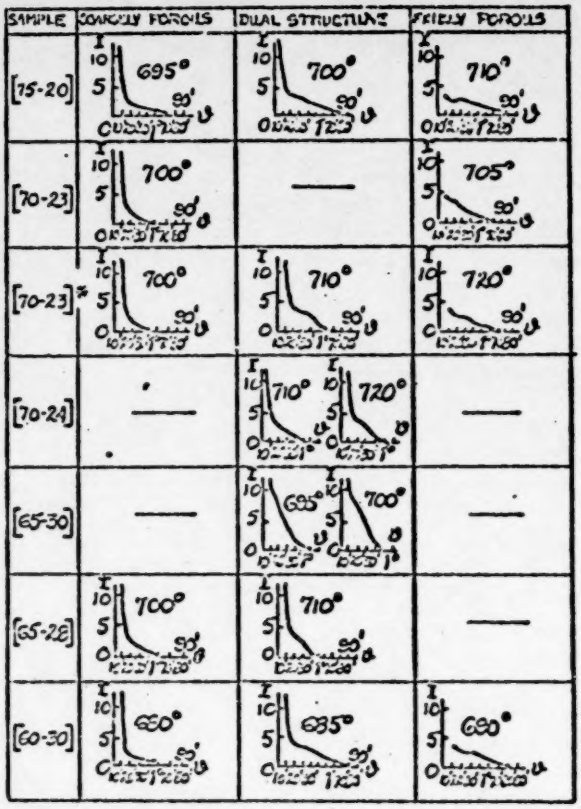

Fig. 6. Intensity curves for porous glasses.

Investigation by low-angle scattering of X-rays applied to porous glasses prepared from original glasses varying in composition and thermal history has therefore enabled us to determine the dimensions of the cells of the silica skeleton and to establish a definite relationship between these dimensions and the opalescence of the original glass. We must again emphasize that we are concerned here with the cells or channels in the silica skeleton, and not with the finer pores between the highly dispersed particles of secondary silicic acid, which may be formed, under certain conditions, within the channels of the basic skeleton.

3. Electron-microscope method**

In electron-microscope investigations of the structure of porous glasses various difficulties arise. The main difficulty is that the dimensions of the pores of porous glasses are generally beyond the limits of resolution of the microscope. Even when the pore dimensions are sufficiently great, it is still far form easy to obtain a good clear photograph: only the pores that penetrate right through the particle of porous glass and are oriented in the direction of the electron beam, i.e., perpendicular to the plane of the image, are visible on the election micrographs.

There is frequently a gray background on the micrographs. This probably arises from the presence of very finely dispersed particles of silicic acid, which cover the collodion film as a continuous layer, so that it is not completely transparent to elections. Finally, when porous glasses are being examined, a displacement is often observed in the image on the screen of the microscope; this is associated with the formation of a charge on the surface of the particles of the porous glass under the action of the electron beam. This displacement results in a certain diffuseness in the outlines of the particles and pores in the electron micrographs..

TABLE 2

Composition of the original glass, mole %			Original glass opalescent		Original glass clear			
			temperature of treatment of original glass (°C)	mean radius of main channels (A)	temperature of treatment of original glass (°C)	radius of main channels		
SiO_2	B_2O_3	Na_2O				from "tail" of curve (A)	from position of maximum (A)	mean radius (A)
75	20	5	695	> 130	715	37	43	40
70	24	6	–	–	720	60	62	61
70	23	7	700	> 640	705	45	47	46
65	30	5	–	–	700	55	63	59
65	28	7	700	> 165	710	80	78	79
60	30	10	680	> 200	690	37	39	38

*Crucible glasses, i.e. glasses cooled very slowly after the fusion and therefore having an opalescent, milky appearance.

**The electron-microscope investigations were carried out with the kind cooperation of V. N. Veitsner, to whom the authors express their deep gratitude.

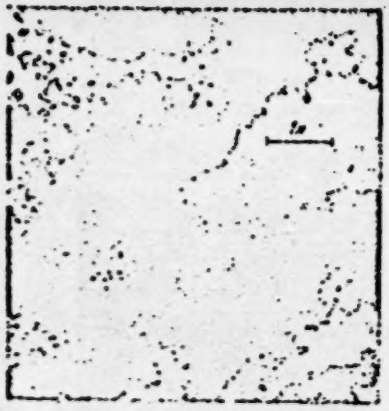

Fig 7. Electron micrograph of the porous glass [Na 70-23]$_{650}$°.

Fig. 8. Electron micrograph of the porous glass [Na 70-23]$_{650}$° after treatment with 0.5 N KOH

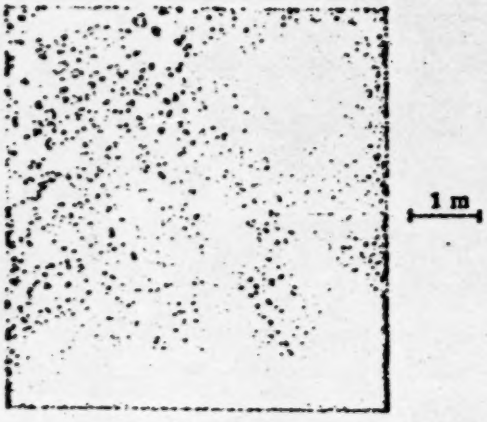

Fig. 9. Electron micrograph of the porous glass [Na 70-23]$_{650}$°, after treatment with 0.5 N KOH.

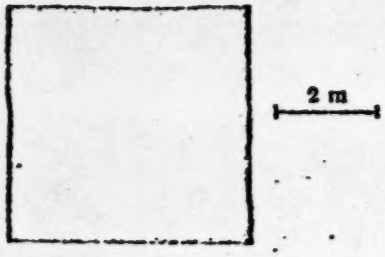

Fig. 10. Electron micrograph of the porous glass [Na 70-23]$_{760}$°.

The conditions under which the specimen is prepared, particularly the degree of grinding, must be selected with due regard for the characteristics of the porous structure of the sample under investigation. When suitable conditions are selected, it is possible to obtain micrographs which reveal the peculiar features of the structure and which enable an estimate to be made of the pore radii of porous glasses. Specimens were prepared for investigation under the electron microscope by applying suspensions of porous-glass powders of various dispersities to special grids carrying collodion films. They were washed with water in test tubes by decantation.

The electron micrograph in Fig. 7 shows particles of the porous glass [Na 70 −23]$_{525}$°; the original glass was clear. On the photograph the particles of porous glass appear to be nonporous, in spite of the fact that adsorption data indicate that more than 20% of the volume of a particle consists of pores. The explanation is that the pores are too small to be resolved by the electron microscope.

It follows from the adsorption measurements that the predominating pore radius is about 14 A and that there are no pores of radius greater than 20 A in this porous glass [7].

The electron micrograph in Fig. 8 is of the product obtained by treating the same porous glass with 0.5 N KOH for two hours. Numerous pores, fairly constant in size, are clearly visible on the photograph; they form a thin-walled honeycomb-like structure. From the micrograph in Fig. 8 the pore radius characteristic of the honeycomb structure can be estimated approximately at the value of 150 A°. According to the adsorption results the most probable value of the radius is 65 A, and according to the X-ray results 46 A.

Quite a different picture is given of alkali-treated porous glasses prepared from an opalescent glass. The electron micrograph in Fig. 9 (see plate, p. 184) is of the porous glass [Na 70 −23]$_{525}$° after treatment in 0.5 N KOH for two hours. This photograph differs from the preceding ones in that it is impossible to detect the presence of a thin-walled honeycomb structure formed from comparatively fine pores. Instead, it can be seen that many of the large particles contain pores and cavities of considerable size and irregular form separated by thick walls. It is a characteristic feature that in this case the smaller particles have no visible pores, but, as judged by their outlines, appear to be pieces that have broken away from the walls of the coarsely porous structure during the comminution of the grains of porous glass which occurred when it was ground in the preparation of the specimen. From the photograph (Fig. 9), the radii of the pores may be estimated at 300-500 A. These values are in good agreement with the results of adsorption and X-ray measurements.

The micrograph in Fig. 10 is of particles of porous glass prepared from strongly opalescent glass Na 70 −23 (heated-treated at 700°) by the usual treatment with 3 N HCl. This sample was not treated with alkali. Adsorption measurements indicated that this porous glass has a uniform finely porous structure having pores of radius 8 A approximately. For this glass, as for those already considered, the adsorption method measures the radius of the pores in the secondary fine structure formed within the coarser structure of the silica skeleton, which can be determined by the adsorption method only after the glass has been treated with alkali. When, however, this sample was investigated by the low-angle X-ray scattering method, very large channels separated by thick walls were detected. On the electron micrograph also, pores of radius greater than 500 A are visible on some of the particles. The photograph as a whole is characterized by a fairly continuous background, which probably arises from very finely dispersed SiO_2 particles forming a thin layer on the collodion film. We are inclined to the view that this finely dispersed SiO_2 is formed by the breakdown of the secondary fine structure in some of the cells of the silica skeleton during grinding of the glass powder in a water medium in an agate mortar and during the sedimentation of the suspension. The large pores seen on the photograph are probably cells of the silica skeleton, which have been revealed here even before the glass has been treated with alkali. Hence, the electron-microscope investigations also show that there is a difference in the structure of porous glass prepared from opalescent and nonopalescent sodium borosilicate glasses.

SUMMARY

1. An investigation of porous glasses by three independent methods (by adsorption measurements, by the low-angle scattering of X-rays, and by the electron microscope) has revealed that they contain two structures: the coarser structure of the basic (silica) skeleton, and the finely porous structure formed of highly dispersed silicicic acid within the channels of the skeleton.

2. The basic skeleton of porous glasses prepared from original glasses that are opalescent always contains channels, the dimensions of which are about ten times as great as those of the channels in porous glasses prepared from clear glasses.

3. When the original glasses are opalescent, the channels may be more than 1000 A in diameter, whereas

°This value must be regarded as somewhat high as a result of difficulties in measuring the diameters of the pores, which, in the case of fine particles, have diffuse outlines on the photograph.

when the original glasses are clear the channels are 80-160 A in diameter. The pores of the highly dispersed silicic acid are not more than 20-40 A in diameter.

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** " " " " p. 19.

SYSTEMS CONTAINING HYDROGEN PEROXIDE AT HIGH CONCENTRATION.

COMMUNICATION 8. THERMAL CHARACTERISTICS AND STABILITIES OF SOLID PHASES OF THE SYSTEM $NaOH - H_2O_2 - H_2O$

S. Z. Makarov and N. K. Grigoryeva

In a study of the 0° isotherm of the system $NaOH - H_2O_2 - H_2O$ [1] we have shown that solid phases of the peroxide type, $Na_2O_2 \cdot 8H_2O$ and $Na_2O_2 \cdot 2H_2O_2 \cdot 4H_2O$ are present. In the literature [2] the second of these compounds $Na_2O_2 \cdot 2H_2O_2 \cdot 4H_2O$ is sometimes regarded as a hydroperoxide derivative $NaOOH \cdot 0.5H_2O_2 \cdot 2H_2O$, since $Na_2O_2 \cdot 2H_2O_2 \cdot 4H_2O = 2[NaOOH \cdot 0.5H_2O_2 \cdot 2H_2O]$. This compound was prepared by vacuum evaporation of a solution containing 3.5-4.0 equivalents of H_2O_2 per equivalent of NaOH. The precipitated crystals were fine and clear, but gradually became opalescent. They effloresced over H_2SO_4, losing their water of crystallization and being converted into the compound $Na_2O_2 \cdot 2H_2O$, which may be treated as $2(NaOOH \cdot 0.5H_2O_2)$ or $Na_2H_4O_4$. The question arose of the synthesis of the "parent" substance, the so-called sodium hydroperoxide NaOOH.

As is well known, sodium hydroperoxide was first prepared by Tafel in 1894 [3] by the action of absolute alcohol on solid sodium peroxide:

$$Na_2O_2 + C_2H_5OH \rightarrow C_2H_5ONa + NaOOH$$

and by mixing Na_2O_2 powder with an ice-cooled mixture of C_2H_5OH and HCl:

$$Na_2O_2 + HCl + C_2H_5OH \rightarrow NaOOH + NaCl + C_2H_5OH.$$

It was noted that when warmed even very slightly the compound decomposed with evolution of oxygen: $2NaOOH \rightarrow 2NaOH + O_2$; and when it was dissolved in water: $NaOOH + H_2O \rightarrow NaOH + H_2O_2$.

Tafel called the compound NaOOH "natryl hydrate". Wolffenstein and Peltner [4] called it "trioxide hydrate" and prepared it by the action of a concentrated alcoholic solution of hydrogen peroxide on sodium ethoxide:

$$NaOC_2H_5 + H_2O_2 \rightarrow NaOOH + C_2H_5OH.$$

It should be noted, however, that although the NaOOH compounds obtained by Tafel and by Wolffenstein and Peltner were identical in composition, they behaved differently towards carbon dioxide.

Tafel's NaOOH was the more stable. D'Ans and Friederich [5] prepared NaOOH by the same method, using 93% H_2O_2. Their product always contained an excess of H_2O_2 and a little H_2O. For the purpose of comparison with the solid phases that we have found for the 0° isotherm of the system $NaOH - H_2O_2 - H_2O$, we have synthesized two samples of sodium "hydroperoxide" by Tafel's method.

EXPERIMENTAL

Heating Curves

a) Sodium Peroxide Octahydrate $Na_2O_2 \cdot 8H_2O$ (Fig. 1). Composition: active oxygen 6.70%, Na_2O 27.30%, H_2O 66.0%. When the $Na_2O_2 \cdot 8H_2O$ was heated to 60-65°, a small endothermic effect was observed. This was not associated with melting or change in composition, but corresponded to the removal of alcohol and ether. At 110-115° a large endothermic effect was observed. At this temperature the substance liquefied, being decomposed with complete loss of active oxygen and undergoing dissolution in the water of crystallization, forming the dihydrate of sodium hydroxide $NaOH \cdot 2H_2O$ of composition Na_2O 37.27% and H_2O 62.73%. When heating was continued until the temperature attained 520°, anhydrous sodium hydroxide of composition Na_2O 74.83% and H_2O 25.17% was obtained.

b) "Sodium Hydroperoxide" $2NaOOH = Na_2O_2 \cdot H_2O_2$ (Fig. 2) had the following composition (%:

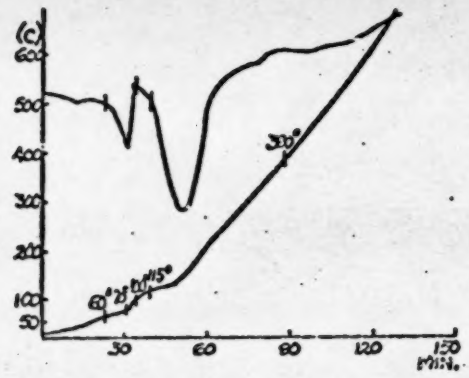

Fig. 1.

First sample:

active oxygen	23.73	NaOOH	82.28
Na_2O	55.44	NaOH	11.14
H_2O	20.83	H_2O	6.58

Second sample:

active oxygen	23.9	NaOOH	83.8
Na_2O	59.83	NaOH	15.7
H_2O	16.27	H_2O	0.5

On the heating curves two thermal effects were detected by the differential method: the first, at 55-65°, was exothermic and was associated with the evolution of active oxygen — not the whole of it, but only the part corresponding to the hydrogen peroxide, if we take the formula to be $Na_2O_2 \cdot H_2O_2$. At this temperature the substance began to cake together and it became close in composition to sodium peroxide monohydrate $Na_2O_2 \cdot H_2O$ (active oxygen 14.29%, Na_2O 63.41%, and H_2O 22.3%). The second seffect — an endothermic one, occurred at about 300° and corresponded to liquefaction. The form of the heating curve would lead us to suppose that the most probable formula for the compound is $Na_2O_2 \cdot H_2O_2$, and not NaOOH.

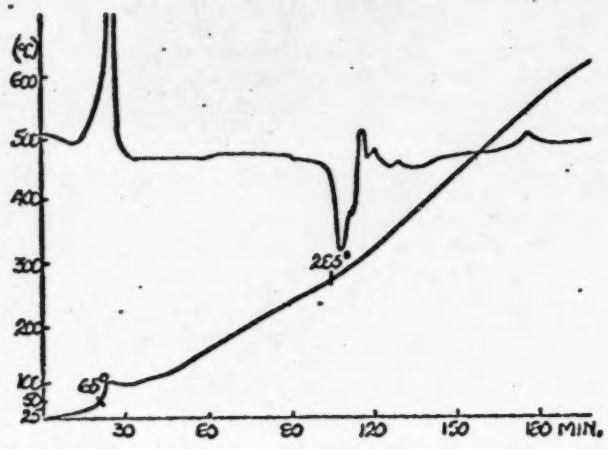

Fig. 2.

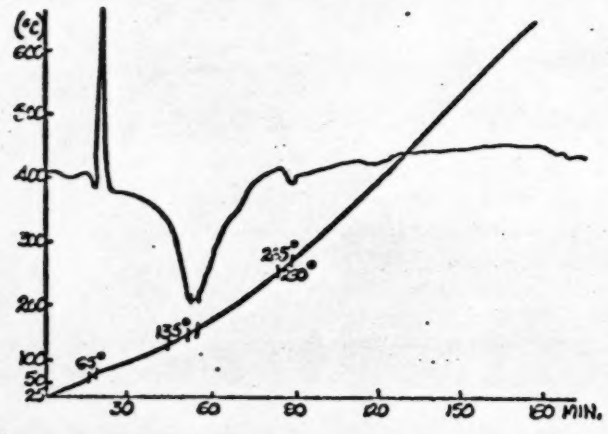

Fig. 3.

c) Sodium Peroxide Perhydrate

$NaOOH \cdot 0.5H_2O_2 = Na_2O_2 \cdot 2H_2O_2 \cdot 4H_2O$ (Fig. 3). Composition: active oxygen 21%, Na_2O 23.54% and H_2O 55.46%. The heating curve showed two effects. The first was endothermic and occurred at 60-65°. The substance then lost the whole of its active oxygen, both that of the hydrogen peroxide and that of the sodium peroxide, which dissolved with decomposition in the water of crystallization. The substance took up the following composition: no active oxygen, Na_2O 34.91%, H_2O 65%. This corresponds approximately to a hydroxide hydrate of the formula $NaOH \cdot 3.5H_2O$, which has the composition Na_2O 30.10%, H_2O 69.90%. At 135° there was an endothermic effect, after which the substance took up the composition corresponding to $NaOH \cdot H_2O$.

Thermal Stabilities of the Compounds

a) Sodium Peroxide Octahydrate

$Na_2O_2 \cdot 8H_2O$. The thermal stability of $Na_2O_2 \cdot 8H_2O$ was investigated at 42° and 62°. For this purpose a weighed amount of it was placed in a test tube having a side tube. The test tube was closed with a stopper carrying a thermometer, and it was then placed in a bath of a substance having a boiling point equal to the desired experimental temperature. The side tube was connected, through a U-tube containing successive columns of soda lime and calcium chloride, to a buret filled with water. The rate at which the substance decomposed was extimated by observations on the volume of water displaced by oxygen per unit time.

Temperature 42°

The original substance, sodium peroxide octahydrate, contained 6.18% of active oxygen and 25.3% of Na_2O; the amount taken was 6.8546 g. The test for thermal stability was carried out at 42° for 1 hour 30 minutes at 767 mm, the room temperature being 15°.

During the first ten minutes the evolution of oxygen was insignificant (1.4 ml), and it then stopped altogether (Table 1). After the experiment the substance contained 5.57% of active oxygen and 24.58% Na_2O, and the loss in weight was 0.0244 g. It may be considered that $Na_2O_2 \cdot 8H_2O$ is stable at 42°.

Temperature 62°

The original substance contained 6.18% of active oxygen and 25.3% of Na_2O; the amount taken was 6.0386 g; room conditions were 763 mm and 15°. The experiment was continued for three hours at 62°. After the experiment the substance contained 26.55% of Na_2O, and active oxygen was completely absent. The loss in weight was 0.3750 g and the amount of water that separated was 0.0018 g. The final product was a clear solution.

TABLE 1

Time (minutes)	Temperature (°C)	Actual amount of oxygen (ml)	Amount of oxygen at NTP (ml/g)
5	28	1.0	0.13
10	38	1.4	0.19
20	40	1.4	0.19
30	41	1.4	0.19
90	41	1.4	0.19

TABLE 2

Time (minutes)	Temperature (°C)	Amount of oxygen		
		actual (ml)	at NTP (ml/g)	Percentage of original oxygen
10	40	2.0	0.31	0.71
20	55	9.0	1.42	3.26
30	62	29.2	4.66	10.26
40	63	59.2	9.33	21.5
50	63	86.0	13.56	31.3
60	62	112.4	17.7	41.0
70	61	140.0	22.0	51.0
80	59	162.0	25.5	59.1
90	59	185.0	29.1	67.5
100	59	222.0	35.0	81.0
110	61	250.0	39.4	91.2
120	62	267.0	42.1	97.4
130	62	270.6	42.7	98.8
150	61	271.2	42.8	99.0
180	61	271.2	42.8	99.0

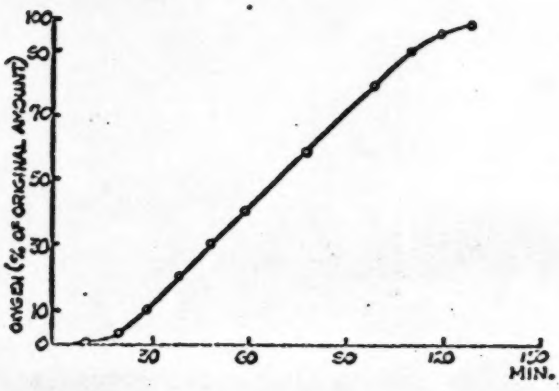

Fig. 4.

Table 2 gives the results of this experiment, and Fig. 4 shows the decomposition curve. At 62°, therefore, $Na_2O_2 \cdot 8H_2O$ is completely decomposed. According to the published results of Jaubert [6], at 30° $Na_2O_2 \cdot 8H_2O$ melts in its water of crystallization, it begins to decompose with evolution of oxygen at 30-40°, and it decomposes completely at 80-100°. Our experiments present a different picture. At 42° sodium peroxide octahydrate did not liquefy and only a very small amount of oxygen was evolved in the first few minutes. It was very stable in spite of the fact that its oxygen and Na_2O contents did not have quite the theoretical values. At 62°, complete liquefaction and decomposition of the octahydrate occurred in 90 minutes.

b) "Sodium Hydroperoxide" $Na_2O_2 \cdot 2H_2O_2 \cdot 4H_2O$

Temperature 30°

The original substance contained 15.3% of active oxygen and 21.91% of Na_2O; the amount taken was 6.831 g. The room conditions were 743 mm and 16°. A preliminary experiment was carried out for three days, the temperature being 20° for periods at the beginning and end of this time, and at 13-15° for the intervening 2.5 days.

After the experiment the substance contained 12.47% of active oxygen and 22.10% Na_2O. The loss in weight was 0.2992 g, and the amount of moisture that separated was 0.0112 g. The decomposition results are given in Table 3, from which it will be seen that the compound is still fairly stable at 30°. It gives up only 18.5% of its original active oxygen, and is converted at 30° into a stable compound containing 12.47% of active ogygen.

TABLE 3

Time (minutes)	Temperature (°C)	Amount of oxygen		Time (minutes)	Temperature (°C)	Amount of oxygen	
		actual (ml)	at NTP (ml/g)			actual (ml)	at NTP (ml/g)
10	30	2.2	0.29	150	35	48.7	6.5
20	31	3.8	0.50	180	33	60.5	8.17
30	31	5.3	0.71	210	32	70.0	9.40
40	31	7.1	0.96	240	31	77.0	10.40
50	31	9.9	1.30	270	31	90.3	12.1
60	31	12.9	1.75	300	31	103.5	13.9
70	31	15.3	2.06	330	31	109.0	14.6
80	31	18.1	2.44	2.5 days	13-15	129.0	17.4
100	31	24.5	3.30	+120	31	132	17.8
130	31	33.3	4.4	+240	31	132	17.8

Temperature 42°

Two experiments were carried out at this temperature. In the first a substance containing 15.30% of active oxygen and 21.94% Na_2O was used, and in the second the substance used contained 9.84% of active oxygen and 26.23% of Na_2O (the second substance had partially decomposed). The results of the first experiment are given in Table 4, and the results of the second are given in Table 5. Fig. 5 gives the decomposition curves for the two substances. In the first experiment the product finally contained 7.06% of active oxygen and 26.26% of Na_2O. In both experiments self-heating occurred with rise in temperature to 57°.

TABLE 4

Time (minutes)	Temperature (°C)	Amount of oxygen		
		actual (ml)	at NTP (ml/g)	Percentage of original oxygen
10	42	6.0	1.67	1.63
20	44	29.0	8.14	8.00
30	44	57.0	16.0	14.9
40	44	87.0	24.4	22.8
50	52	128.0	33.1	30.9
60	57	192.0	53.9	50.4
70	47	205.0	57.4	53.7
90	43	207.6	58.3	54.4
120	43	207.6	58.3	54.4

TABLE 5

Time (minutes)	Temperature (°C)	Amount of oxygen		
		actual (ml)	at NTP (ml/g)	Percentage of original oxygen
5	37.5	7.5	1.6	2.3
10	41.0	20.0	2.9	4.2
15	42.5	37.0	5.4	7.8
20	43.5	57.0	8.7	12.6
25	45.0	85.0	12.4	16.0
30	57.0	153.0	22.5	32.7
35	55.0	178.0	26.1	37.9
40	49.0	183.0	26.9	39.1
45	44.0	185.0	27.1	39.3
50	42.0	185.0	27.1	39.3
60	42.0	185.0	27.1	39.3
90	37.0	185.0	27.1	39.3

Temperature 57°

At 57° intense self-heating occurred, and threre was rapid liquefaction with much frothing. It was difficult to follow the progressive decompostion of the substance. Table 6 gives the results of this experiment. It will be seen, therefore, that at 30° $Na_2O_2 \cdot 2H_2O_2 \cdot 4H_2O$ decomposes partially with evolution of a part of its active oxygen; at 42° it decomposes with formation of sodium peroxide octahydrate, which is still fairly stable under these conditions; and at 57° it decomposes vigorously with rapid evolution of oxygen.

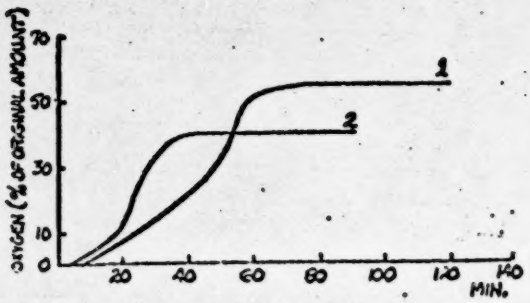

Fig. 5

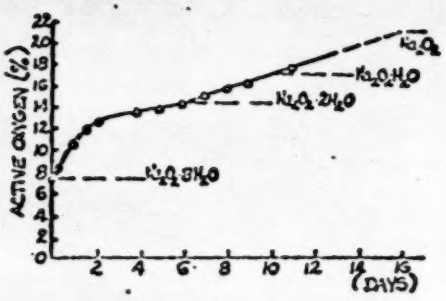

Fig. 6

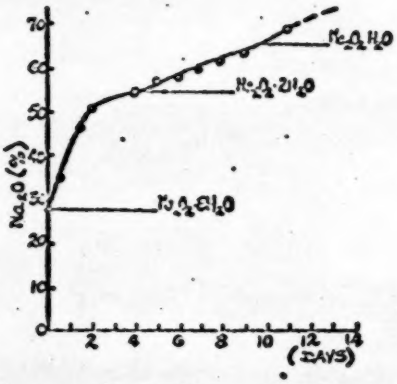

Fig. 7

TABLE 6

Time (minutes)	Temperature (°C)	Amount of oxygen actual (ml)	Amount of oxygen in ml/g
5	39	5	0.84
10	47	35	5.94
15	70	175	29.5
17	63	250	42.1
18	61	270	45.5
19	60	290	48.9
20	58	The substance liquefied and frothed up	

Dehydration of $Na_2O_2 \cdot 8H_2O$*

The experiments on the dehydration of $Na_2O_2 \cdot 8H_2O$ were carried out on crystals (large plates reminiscent of mica) prepared from $NaOH \cdot H_2O$ and H_2O_2. The crystals of $Na_2O_2 \cdot 8H_2O$ were carefully pressed off on the filter and then placed in a thin layer in a Petri dish, which was placed over sulfuric acid in a vacuum desiccator. At intervals of 0.5-1 day samples were taken for analysis for the active oxygen, Na_2O, and H_2O contents, the desiccator being evacuated after removal of the sample. As the dehydration process proceeded, the large clear crystals of $Na_2O_2 \cdot 8H_2O$ were converted into small pale-yellow opaque crystals, and the yellowish color characteristic of anhydrous sodium peroxide gradually became more intense. The final product was found by analysis to have a composition close to $Na_2O_2 \cdot H_2O$. The analytic results for this experiment, which lasted for eleven days, are given in Table 7.

The variation of the content of active oxygen with time is shown in Fig. 6, and the variation in the Na_2O content in Fig. 7. Both diagrams show clearly that the dehydration of $Na_2O_2 \cdot 8H_2O$ goes as far as $Na_2O_2 \cdot 2H_2O$ in the course of 4-5 days, and as far as $Na_2O_2 \cdot H_2O$ in ten days.

SUMMARY

1. An investigation has been made, with the aid of heating curves, of the thermal stabilities and dehydration behavior of the solid phases found in the ternary system $NaOH - H_2O_2 - H_2O$ at 0°, namely $Na_2O_2 \cdot 8H_2O$ and $Na_2O_2 \cdot 2H_2O_2 \cdot 4H_2O$, and also of the so-called "sodium hydroperoxide" NaOOH or $Na_2O_2 \cdot H_2O_2$, which was synthesized by Tafel's method.

2. The compound $Na_2O_2 \cdot 8H_2O$ is undoubtedly a hydrated form of sodium peroxide. This view is confirmed by the occurrence of endothermic dehydration effects, and by the curves for the dehydration of $Na_2O_2 \cdot 8H_2O$, which pass through the stages $Na_2O_2 \cdot 8H_2O$, $Na_2O_2 \cdot 2H_2O$, and $Na_2O_2 \cdot H_2O$.

3. The compound $Na_2O_2 \cdot 2H_2O_2 \cdot 4H_2O$ is of lower stability. Its heating curve has a very marked exothermic maximum at 60-65° characteristic of perhydrate compounds. The temperature at which complete decomposition occurs is the same as the decomposition temperature of $Na_2O_2 \cdot 8H_2O$.

4. The existing data on the properties of the so-called "sodium hydroperoxide" NaOOH support the view that this compound should be regarded as $Na_2O_2 \cdot H_2O_2$.

* The experimental work was carried out by I. F. Bulycheva.

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TABLE 1

t°	h · 10²	π	h · 10²	π	h · 10²	π	h · 10²	π	h · 10²	π
1	2	3	4	5	6	7	8	9	10	11
				Diethyl ether						
				At t = 25°, p_0 = 550 mm Hg; At t = 40°, p_0 = 955 mm Hg						
25°	0.085	0.6	1.32	10.8	4.16	21.5	20.0	37.4	42.7	47.7
	0.182	2.3	2.21	13.9	4.67	21.6	20.8	38.0	48.0	51.3
	0.352	4.0	2.18	14.2	6.60	24.5	24.0	39.6	51.5	51.3
	0.368	3.8	2.63	16.0	7.25	25.6	30.2	42.8	57.0	52.8
	0.638	6.2	2.82	16.5	8.67	27.3	30.9	42.9		
	0.930	8.2	3.40	18.3	9.55	28.7	36.3	44.8		
	1.23	10.3	3.60	19.4	15.5	33.5	41.0	47.1		
40°	0.0014	0.1	0.793	5.7	2.70	15.3	6.32	23.3	22.9	37.8
	0.191	2.5	1.26	9.7	3.17	17.5	6.45	23.6	25.1	39.2
	0.526	4.7	1.95	12.7	3.32	17.8	6.45	24.1	26.4	40.4
	0.575	4.7	2.19	12.5	4.03	18.9	11.5	30.0	29.5	41.6
	0.725	6.1	2.19	19.9	5.00	20.9	17.4	33.6		
				Acetone						
				At t = 25°, p_0 = 255 mm Hg						
25°	0.36	1.5	2.28	10.0	6.62	18.1	22.3	32.3	51.2	51.2
	0.48	2.4	3.05	10.6	7.05	17.4	23.9	37.2	53.5	51.7
	0.76	4.3	3.20	12.3	8.39	19.1	33.2	40.6	60.0	55.9
	1.13	5.2	3.47	11.8	9.33	20.7	35.6	42.1	66.2	59.5
	1.16	5.7	4.38	13.5	11.0	21.9	41.8	45.5	73.4	61.4
	1.35	6.9	5.27	15.6	13.9	25.0	45.5	49.2	79.9	65.2
	2.22	7.9	5.70	16.2	17.4	28.5	50.3	51.4	100.0	75.2
				Heptane						
				At t = 15°, p_0 = 27.55 mm Hg. At t = 25°, p_0 = 47.65 mm Hg. At t = 40°, p_0 = 92.05 mm Hg						
15°	0.192	10.5	1.58	26.1	6.68	40.7	26.9	54.4	71.3	66.9
	0.203	11.0	1.58	28.7	7.65	40.9	31.3	56.5	79.5	67.9
	0.224	11.5	2.18	29.8	9.32	42.7	34.2	57.6	95.5	71.6
	0.406	15.4	3.46	33.7	13.5	47.9	37.6	59.4	100.0	72.8
	0.515	16.6	3.96	33.9	14.1	47.9	41.0	60.1		
	0.632	17.7	4.82	37.5	17.7	49.4	49.7	61.8		
	0.660	18.5	5.30	38.8	20.4	55.1	60.5	64.9		
	1.26	23.9	5.80	39.9	23.2	53.2	65.4	65.9		
25°	0.124	7.7	0.635	17.2	4.65	35.0	13.5	45.3	40.0	56.7
	0.136	8.5	0.735	17.7	5.82	36.0	14.8	45.4	46.0	57.9
	0.195	10.4	0.872	20.4	6.50	37.3	18.0	47.1	57.4	60.0
	0.196	10.3	1.01	21.4	8.55	40.0	19.8	47.6	60.7	61.3
	0.236	10.8	1.66	25.7	8.97	39.2	21.5	49.0	73.0	63.4
	0.258	12.2	2.00	27.7	9.40	39.7	23.6	50.4	93.6	68.6
	0.318	13.3	2.94	31.3	10.2	42.7	28.4	52.8	96.0	69.5
	0.477	16.0	3.40	32.2	12.3	45.2	30.0	53.1	98.0	71.0
40°	0.108	6.0	2.64	26.2	6.12	33.1	11.6	38.6	21.4	43.7
	0.195	7.8	3.06	28.0	6.40	33.7	12.5	39.0	27.4	47.2
	0.326	9.9	3.94	30.5	7.00	34.5	13.5	39.5	32.6	49.1
	0.445	12.0	4.05	29.4	7.69	35.2	15.0	40.5	35.6	50.6
	0.640	14.1	5.15	32.2	8.05	35.8	15.7	41.0		
	1.14	18.0	5.32	32.2	8.82	36.4	17.2	41.9		
	1.86	23.2	5.58	32.3	11.6	37.9	19.8	43.5		

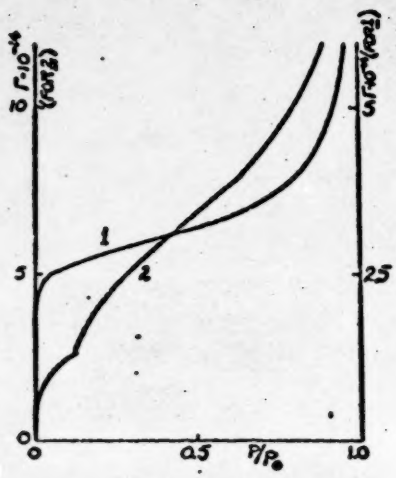

Fig. 1.

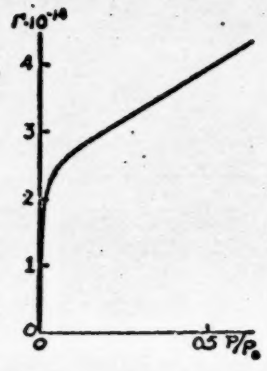

Fig. 2.

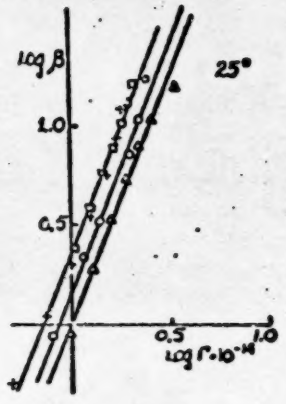

Fig. 3.

(μ_e is the effective dipole moment of a molecule oriented normally to the adsorbent surface). Equation 3 leads to the following equation for the adsorption isotherm:

$$\ln \frac{\Gamma}{p} = \ln H - \frac{7{,}5}{kT}\,\mu_e^2\,\Gamma^{3/2}. \qquad (4)$$

(H is the integration constant). The equation for the surface-pressure isotherm corresponding to Equation 3 cannot be obtained analytically in an explicit form.

When an examination is made of adsorption at energetically homogeneous surfaces, it can be shown [7] that the sign of the slope of the adsorption isotherm in its initial part is determined by the sign of the forces of interaction between the adsorbed molecules; repulsive forces should give convex isotherms, and attractive forces should give concave isotherms. The convex isotherms of the substances now under consideration indicate a predominance of repulsive forces in the surface layer, so that for these substances it is logical to use the very simple scheme of dipole interaction described by Equation 3.

For the purpose of the quantitative verification of the applicability of Equation 3, it may be presented in the following form:

$$\log \beta = \log (\pi - kT\Gamma) = \log 4{,}5\,\mu_e^2 + \frac{5}{2}\,\log \Gamma, \qquad (5)$$

(β is the departure of the actual isotherm of state from the ideal isotherm, which would be given by an ideal two-dimensional gas). If we transform the values of π and Γ into the coordinates log β and log Γ, then if Equation 3 is obeyed we must obtain a straight line of slope 5/2, and the intercept on the axis of ordinates will enable the value of μ_e to be determined.

Fig. 3 shows the results of this construction for heptane (□), diethyl ether (○), and acetone (△), calculated from our data, and for toluene (+), calculated from Kemball's data, the straight lines being drawn at the theoretical slope of 5/2. As will be seen from Fig. 3, Equation 3 is closely obeyed in the monomolecular region by these substances. At higher values of Γ the curves depart from straight lines owing to increase in the effectiveness of attractive forces and to transition to polymolecular adsorption.

For these substances, therefore, Equations 1 and 3 are obeyed simultaneously. It is easy to see that this fact follows from the forms of the two equations. Thus, if Equation 1 is presented in the form:

$$\pi = kT\Gamma + kT\Omega\frac{\Gamma^2}{1-\Omega\Gamma}, \qquad (6)$$

it becomes evident that it must approximate closely to Equation 3. Hence, whenever Equation 1 is obeyed, Equation 3 also must be obeyed. From the intersects on the axis of ordinates (Fig. 3), the effective dipole moments were calculated. The resulting values of μ_e are given in Table 2 together with the permanent dipole moments μ and the values of the mean polarizabilities of the molecules, $\bar{b} = 1/3\,(b_1 + b_2 + b_3)$. b_1, b_2, b_3 are the principal axes of the polarization ellipsoid.

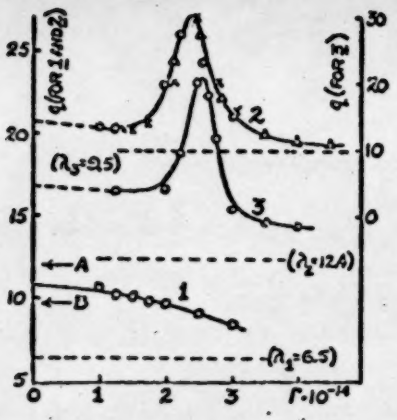

Fig. 5.

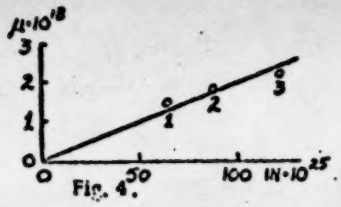

Fig. 4.

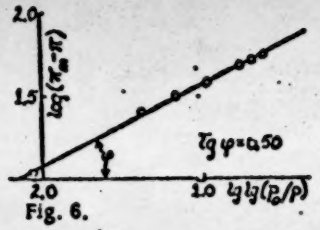

Fig. 6.

We may infer from Table 2 that the electron envelopes of the adsorbed molecules are greatly deformed in the field at a mercury surface, and, as a result of the polarization, electrical moments comparable in magnitude with the permanent dipole moments of polar molecules are induced in these molecules. The value of the induced moment is proportional, to a first approximation, to the mean polarizability of the molecule, i.e. $\mu_e \approx C\bar{b}$, as shown in Fig. 4 (1 is acetone, 2 is ether, and 3 is toluene). When we take into consideration that it is not the polarizability $\bar{b}$ that should be used in these considerations, but the polarizability corresponding to the orientation of the molecules in the surface layer, and that the value of μ_e is determined by this method with low accuracy, the approximate proportionality between μ_e and $\bar{b}$ must be regarded as a weighty argument in favor of the concepts that we have discussed. In this connection we may note that Mignolet [8] has recently shown that surface potentials of +0.16–0.27 V occur when CH_4, C_2H_2, C_2H_4, and C_2H_6 are adsorbed at a mercury surface, and he concluded that the molecules of these substances are strongly polarized in the field of the mercury surface.

The low value of μ_e for acetone is noteworthy, for it is considerably less than the permanent dipole moment μ = 2.73 D. This fact probably indicates that the acetone molecule, when adsorbed, makes contact with the mercury surface with three C atoms and an O atom, so that the permanent moment, which is localized in the CO group, is oriented parallel to the mercury surface.

With a view to a further verification of Equation 3 and of the proposed model of a nonlocalized adsorption layer, we have calculated the curves showing the dependence of the differential heats of adsorption on the coverage of the surface for the case of diethyl ether. For this purpose we applied the Clausius-Clapeyron equation to the 15° and 25° isotherms. The results of these calculations are shown by the circles on Curve 1 in Fig. 5

TABLE 2

Substance	μ_e (Debye units)	μ (Debye units)	$\bar{b} \cdot 10^{25}$ CGS units
Toluene	2.2	0.4	123
Heptane	2.2	0.0	—
Diethyl ether	1.8	1.14	88
Acetone	1.5	2.73	64

If we assumed that to a first approximation the value of μ_e is independent of temperature, then finding $(d \ln p/dT)_\Gamma$, from Equation 4 and substituting this derivative in the Clausius-Clapeyron equation, we obtain the following equation from the dependence of the differential heat of adsorption q on Γ:

$$q = \left(\frac{d \ln H}{dT}\right)_\Gamma - 7.5\,\mu_e^2 N \Gamma^{3/2} = q_0 - 7.5\,\mu_e^2 N \Gamma^{3/2}, \quad (7)$$

(N is Avogadro's number).

For the given case, Equation 7 enables us to determine the variation of q with the coverage of the surface from a single adsorption isotherm. Curve 1 in Fig. 5 was constructed with the aid of Equation 7. The values of $q_0 - q$ calculated by Equation 7 were represented as a function of Γ, and the resulting curve was displaced in a direction parallel to the axis of ordinates until it coincided with the points indicated by the circles. Simultaneously, the values of Γ were expressed in the ordinates $\log(\Gamma/p)$ and $\Gamma^{3/2}$ for 15° and 25°, and from the linear graphs obtained (corresponding to Equation 4) the intercepts H_1 and H_2 on the axis of ordinates were determined. From these intercepts the value of $q_0 \approx \Delta \ln H/\Delta T$ was found. This calculation of q_0 cannot be particularly accurate owing to the closeness of H_1 and H_2 in value. The arrows A and B in Fig. 5 indicate the limits of possible error in the determination of q_0. Hence, the curve $q = q(\Gamma)$ in Fig. 5 confirms the validity of Equation 3 and of the assumption of the substantial independence of μ_e on temperature.

The values of q were calculated also for heptane. Results of the calculation from the Clausius-Clapeyron equation are indicated by circles (calculated from the 15° and 40° isotherms) and triangles (15° and 25° isotherms) on Curve 2 in Fig. 5. For heptane the curve $q = q(\Gamma)$ is characterized by a sharp maximum at a coverage θ of about 1. In order to be more certain that this maximum is not the result of errors in the calculation of Γ, we calculated q directly from two $\pi = \pi(\lg h)$ curves corresponding to different temperatures. For this purpose,

we calculated the integral heats of adsorption Q from William's equation [9]

$$Q = \pi - T\left(\frac{d\pi}{dT}\right)_p \qquad (8)$$

and then found the corresponding values of the differential heats $q = \frac{dQ}{d\Gamma}$ by graphical differentiation of the curve obtained, $Q = Q(\Gamma)$; these values are shown by crosses on Curve 2 in Fig. 5. Comparison of the results of the two methods of calculation leaves no doubt about the reality of this maximum. A similar maximum was obtained when q was calculated from the 25° and 50° isotherms $\pi = \pi(\log h)$ for butyl alcohol (Curve 3 in Fig. 5). It should be noted that the initial heats of adsorption of the two isomers, butyl alcohol and diethyl ether, differ by approximately 6 kcal per mole, i.e. by an amount of the same order as the difference in the latent heats λ, and also, probably, as the energy of the hydrogen bond in butyl alcohol.

In recent years there have been several papers relating to the investigation of adsorption at homogeneous surfaces, and in these maxima have been found on the $q = q(\Gamma)$ curves for a coverage of $\theta \approx 1$, and sometimes for $\theta \approx 2$. We may mention here papers by Orr [10], who appears to have been the first to observe such maxima in a study of the adsorption of argon, oxygen, and nitrogen on potassium chloride and cesium iodide, by Rhodin [11], who examined the adsorption of nitrogen at the surface of copper monocrystals, and by Beebe and Young [12], who made a calorimetric study of the adsorption of argon on Graphon, a crystalline preparation of carbon, and found maxima at $\theta = 1$ and $\theta = 2$ on the $q = q(\Gamma)$ curves. Also, in an investigation by one of the authors of this paper and Serpinsky [13], a maximum value of q was found for the adsorption of nitrogen on sodium chloride at −195°.

A consideration of these examples, together with the examples of maxima in the adsorption of heptane, butyl alcohol, and water on mercury, tends to suggest that the appearance of maxima in the region of $\theta = 1$ on $q = q(\Gamma)$ curves for adsorption at homogeneous surfaces is the rule, rather than the exception. At high degrees of coverage Van der Waals attractive forces between adsorbed molecules begin to be significant, for they become appreciable when the intermolecular distances become small, and they grow much more rapidly than the electrostatic forces of dipole repulsion.

In conclusion we will make a somewhat more detailed examination of polymolecular adsorption at a mercury surface, taking the example of methanol, for which such adsorption is particularly characteristic. For this substance, which has small polar molecules, the adsorbed film is already 8-10 layers thick when $h = 0.9$. In view of the nonapplicability of Brunauer, Emmett, and Teller's equation for polymolecular adsorption to the adsorption isotherms of the substances that we have studied, it is of interest to determine to what extent the data for methanol satisfy the equation for polymolecular adsorption derived by Frankel [14] and independently by Halsey and Hill (see, for example, [5]), on the assumption that the potential of the interaction forces between a molecule and a plane surface falls off (as suggested by London) with distance according to an inverse cube law. This equation has the form:

$$\ln \frac{p_0}{p} = \frac{K}{\nu^3} \approx \frac{K'}{\Gamma^3} \quad . \qquad (9)$$

(K is a constant, and ν is the number of layers). For thick layers Γ is proportional to ν).

It is readily shown with the aid of the Gibbs adsorption equation that Equation 9 for the adsorption isotherm corresponds to the following surface-pressure isotherm:

$$\log\ (\pi_m - \pi) = \log C + \frac{2}{3}\log\left(\log\frac{p_0}{p}\right). \qquad (10)$$

(C is a constant, and π_m is the value of π when $h = 1$. If Equation 9 is obeyed, then when the experimental values of π in the polymolecular region are expressed in the coordinates $\log(\pi_m - \pi)$, $\log\left(\log\frac{p_0}{p}\right)$, we should obtain a straight line of slope 2/3. Fig. 6 shows the results of the verification of Equation 10 for methanol at 25°. The experimental points fit satisfactorily to a straight line, but its slope is not 2/3, but almost exactly 1/2. It will be readily seen that if the slope is 1/2 we obtain the following equation for polymolecular adsorption instead of Equation 9:

$$\ln \frac{p_0}{p} = \frac{B}{\Gamma^2} \quad . \qquad (11)$$

which differs from Harkins and Jura's equation [15] in the absence of a constant term.

Bowers [16] measured the adsorption of gases on aluminum foil at low temperatures by the gravimetric method, and found that Equation 9 was closely obeyed by nitrogen. Later, however, in a study of the adsorption of

helium on aluminum foil, Bowers [17] showed that the dependence of the thickness Δ of a polymolecular film of helium on the distance d of the given point on the surface of the adsorbent from the level of the liquid helium was given by the formula:

$$\Delta = Kd^{-1/n} \qquad (12)$$

in which n was found to be 2.0 ± 0.3.

Since the relation of the relative pressure over the surface of a liquid to the height d is given by the barometric formula, Equation 12 will reduce to Equation 11 when $n = 2$.

Hence the polymolecular adsorption of methanol on mercury and of helium on aluminum is described by Equation 11, and not Equation 9. On the basis of this result, however, it would be premature to speak of the non-applicability of Equation 9 in the analysis of polymolecular adsorption at smooth surfaces. It is clear that the matter demands further study.

The authors are deeply grateful to V. V. Serpinsky, M. M. Dubinin, B. V. Ilyin, and A. I. Sarakhov for their interest in the work, their valuable advice, and their help in organizing the investigation.

SUMMARY

1. It has been shown that an equation of state derived for nonlocalized adsorption and taking into account the electrostatic repulsive forces between identically oriented dipole molecules is applicable to the adsorption of diethyl ether, acetone, heptane, and toluene on mercury. It has been shown also that when this equation is obeyed Volmer's equation must also be obeyed. The equation has been further verified by calculating the heats of adsorption of diethyl ether.

2. There is reason to suppose that, when acetone, toluene, heptane, and diethyl ether are adsorbed on mercury, dipole moments are induced in the molecules of these substances, and these moments are comparable in magnitude to the permanent moments of polar molecules.

3. There are maxima on the curves showing the dependence of the differential heat of adsorption on surface coverage for heptane, butyl alcohol, and water, and these are found at a degree of coverage of approximately unity.

4. It has been shown that in the polymolecular adsorption of methanol on mercury the equation of Frenkel, Halsey, and Hill is not obeyed and that the experimental data for this case are in close accord with the results of direct measurements of the polymolecular adsorption of helium on aluminum.

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ω-CHLORO CARBOXYLIC ACIDS, AND SOME OF THEIR REACTIONS

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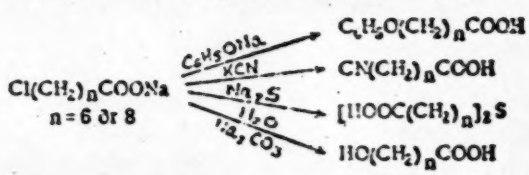
Whereas the higher ω-bromo carboxylic acids $Br(CH_2)_n COOH$ have received fairly detailed investigation and are widely applied in various syntheses, the corresponding ω-chloro carboxylic acids have received comparatively little study, probably because it is considered that the chlorine atom in these compounds is of low reactivity, and also because of the difficulty of preparing them. Recently, however, a convenient method has been found for the synthesis of some of the ω-chloro carboxylic acids. It consists in the hydrolysis of α,α,α, ω-tetrachloroalkanes $Cl(CH_2CH_2)_n CCl_3$ with concentrated sulfuric acid. These chloro compounds are prepared by the reaction of ethylene with carbon tetrachloride under pressure [1, 2], and they give acids having odd numbers of carbon atoms. By this method 5-chlorovaleric, 7-chloroheptanoic, and 9-chlorononanoic acids have been prepared from 1, 1, 1,-5-tetrachloropentane, 1, 1, 1,7-tetrachloroheptane, and 1,1,1,9-tetrachlorononane respectively [1, 3]. In the present investigation we have isolated the succeeding tetrachloroalkanes from the products of the reaction of ethylene with carbon tetrachlorides, and by hydrolysis of these we have prepared 11-chloroundecanoic, 13-chlorotridecanoic, and 15-chloropentadecanoic acids. We have investigated some of the reactions of these ω-chloro carboxylic acids, and have shown that they can be used successfully instead of the corresponding bromo acids. When the ethyl esters of 5-chlorovaleric and 7-chloroheptanoic acids were treated with sodium alkoxide, the corresponding alkoxy esters were obtained. The reaction of the same ethyl esters with sodiomalonic ester in presence of sodium iodide gave high yields of the triethyl esters of 1,1,5-pentanetricarboxylic and 1,1,7-heptanetricarboxylic acids, which yielded pimelic and azelaic acids respectively when hydrolyzed with dilute hydrochloric acid.

It was found that salts of 7-chloroheptanoic and 9-chlorononanoic acids readily reacted in aqueous solution with sodium phenoxide, and with sodium cyanide; they were hydrolyzed in presence of bases into ω-hydroxy carboxylic acids. In collaboration with Petrova [4] we have shown previously that both of these chloro acids readily react with sodium sulfide in aqueous solution and yield the corresponding ω,ω'-thio dicarboxylic acids.

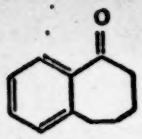


Oxidation of 7-hydroxyheptanoic acid with concentrated nitric acid gave pimelic acid in high yield. Hydrogenation of 7-cyanoheptanoic in ammoniacal solution in presence of Raney nickel yielded 8-aminooctanoic acid. When, however, salts of 5-chlorovaleric acid were treated with sodium phenoxide or sodium cyanide in aqueous solution, the corresponding derivatives were not formed, the product being δ-valerolactone (or 5-hydroxyvaleric acid), which does not react further under these conditions. On the other hand, with the sodium salt of benzenethiol 5-chlorovaleric acid gave a good yield of 5-(phenylthio)valeric acid. It was found that 5-phenoxyvaleric acid could be obtained from 5-chlorovaleric acid only via δ-valerolactone by heating the latter with anhydrous sodium phenoxide at high temperature, the reaction being analogous to the preparation of 4-phenoxybutyric acid from γ-butyrolactone [5].

7-Chloroheptanoic acid was converted into the trimethylbetaine of 7-aminoheptanoic acid, and so, by cleavage of the latter with alkali, into 6-heptenoic acid:

$$Cl(CH_2)_6COOH \rightarrow (CH_3)_3\overset{+}{N}(CH_2)_6COO^- \xrightarrow{NaOH} CH_2=CH-(CH_2)_4COOH + (CH_3)_3N.$$

We have studied the reaction of ω-chloro carboxylic acids with benzene in presence of aluminum chloride. It has been shown previously [6] that 4-chlorobutyric acid reacts with benzene to give 4-phenylbutyric acid. In a similar way, 5-chlorovaleric acid in presence of aluminum chloride at a molar ratio of 1:1 gave a high yield of 5-phenylvaleric acid. When the amount of aluminum chloride was increased, in addition to 5-phenylvaleric acid 1-benzosuberanone was formed:

$$C_6H_6 + Cl(CH_2)_4COOH \xrightarrow{AlCl_3} C_6H_5(CH_2)_4COOH +$$ 

It should be noted that the yield of 5-phenylvaleric acid obtained from 5-chlorovaleric acid was higher than that which has been obtained from δ-valerolactone [7]. Unlike the lower acids, 7-chloroheptanoic, 9-chlorononanoic, and 11-chloroundecanoic acids reacted with benzene in presence of aluminum chloride with isomerization, for the resulting "phenylheptanoic", "phenylnonanoic", and "phenylundecanoic" acids were found to be different from the known 7-phenylheptanoic acid [8], 9-phenylnonanoic acid [9], and 11-phenylundecanoic acid [10] respectively. When the "phenylnonanoic" and "phenylheptanoic" acids were oxidized in acetic acid with chromic anhydride, acetophenone was isolated*, which indicates the presence of the grouping $C_6H_5CH(CH_3)$ in the acids. The structure of the central part of the molecule has not been investigated. It is probable that for these acids reaction proceeds by the scheme:

$$C_6H_6 + Cl(CH_2)_nCOOH \xrightarrow{AlCl_3} C_6H_5\underset{\displaystyle CH_3}{\underset{|}{CH}}-(CH_2)_{n-3}COOH,$$

(n = 6, 8 or 10).

The condensation of 5-chlorovaleryl and 7-chloroheptanoyl chlorides with benzene in presence of aluminum chloride went in the normal fashion and yielded the corresponding ω-chloroalkanophenones:

$$C_6H_6 + ClCO(CH_2)_nCl \xrightarrow{AlCl_3} C_6H_5CO(CH_2)_nCl,$$

(n = 4 or 6).

With the object of characterizing the ω-chloro carboxylic acids discussed above, some of their derivatives were prepared.

EXPERIMENTAL

For the preparation of the α,α,α,ω-tetrachloroalkanes, the reaction of ethylene with carbon tetrachloride was carried out as already described [1].

5-Chlorovaleric Acid was prepared by hydrolysis of 1,1,1,5-tetrachloropentane by the method already described [1,3]. Its amide melted at 78-79° (from benzene).

	Found %:	N 10.45; 10.52
$C_5H_{10}ClNO$.	Calculated %.	N 10.33

Its anilide melted at 108-109° (from benzene).

	Found %:	N 6.67; 6.59
$C_{11}H_{14}ClNO$.	Calculated %:	N 6.63

7-Chloroheptanoic Acid was prepared by hydrolysis of 1,1,1,7-tetrachloroheptane by the method already described [1, 3]. Its ethyl ester boiled at 122-123° (11 mm) and had n_D^{23} 1.4392; d_4^{20} 1.0110; found MR 50.10; calculated MR 50.27.

	Found %:	C 56.24; 56.30; H 8.95; 8.84
$C_9H_{17}ClO_2$.	Calculated %:	C 56.10; H 8.83

Its anilide melted at 85-86° (from benzene).

	Found %:	N 5.83; 5.87
$C_{13}H_{18}ClNO$.	Calculated %:	N 5.86

Its amide melted at 82-83° (from benzene).

	Found %:	N 8.46; 8.48
$C_7H_{14}ClNO$	Calculated %:	N 8.57

9-Chlorononanoic Acid was prepared by hydrolysis of 1,1,1,9-tetrachlorononane by the method already described [1,3]. It melted at 29-30° (from petroleum ether). Its ethyl ester boiled at 136-137° (8 mm) and had

*Oxidation of 5-phenylvaleric acid under like conditions yields 4-benzoylbutyric acid.

n_D^{20} 1.4434; d_4^{20} 0.9854; found MR 59.37; calculated MR 59.51

	Found %:	C 59.72; 59.60; H 9.42; 9.52
$C_{11}H_{21}ClO_2$.	Calculated %:	C 59.84; H 9.58

Its acid chloride boiled at 100-101° (3 mm). Its amide melted at 76-77° (from benzene).

	Found %:	N 7.40; 7.58
$C_5H_{18}ClNO$.	Calculated %:	N 7.32

Its anilide melted at 95-96° (from methanol).

	Found %:	N 5.16; 5.12
$C_{15}H_{22}ClNO$.	Calculated %:	N 5.04

Its nitrile boiled at 105-106° (1.5 mm) and had n_D^{20} 1.4512; d_4^{20} 0.9695; found MR 48.21; calculated MR 48.44.

	Found %:	N 8.22; 8.16
$C_5H_{16}ClN$.	Calculated %:	N 8.07

11-Chloroundecanoic Acid. 1,1,1,11-Tetrachloroundecane boiled at 141-142° (3 mm) and had n_D^{20} 1.4822; d_4^{20} 1.1558; found MR 72.55; calculated MR 72.46.

	Found %:	C 45.06; 45.08; H 6.89; 6.77
$C_{11}H_{20}Cl_4$.	Calculated %:	C 44.96; H 6.80

A mixture of 77 g of the tetrachloroundecane and 250 g of concentrated sulfuric acid (92-93%) was vigorously stirred and heated in a water bath for 90 minutes. In the course of this time almost the theoretical amount of hydrogen chloride was evolved. The reaction mixture was cooled and poured onto ice, and the chloroundecanoic acid was extracted with carbon tetrachloride. The extract was washed twice with water and dried with calcium chloride. When the solvent was removed, the residue crystallized out, but vacuum distillation was found to be essential for the purification of the chloro acid. The yield of 11-chloroundecanoic acid was 41.2 g (71.5%). It boiled at 149-151° (1.5 mm) and melted at 41-42° (the literature [11] gives 39-40°).

	Found %:	C 59.94; 59.82; H 9.43, 9.56
$C_{11}H_{21}ClO_2$.	Calculated %:	C 59.86; H 9.52

Its ethyl ester boiled at 133.134° (3 mm) and had n_D^{20} 1.4469; d_4^{20} 0.9646; found MR 68.68; calculated MR 68.75

	Found %:	C 62.92; 62.90; H 10.05; 10.16
$C_{13}H_{25}ClO_2$.	Calculated %:	C 62.75; H 10.12

Its acid chloride boiled at 133-134° (4.5 mm). Its amide melted at 89-90° (from benzene).

	Found %:	N 6.42; 6.48
$C_{11}H_{22}ClNO$.	Calculated %:	N 6.37

Its anilide melted at 69-70° (from methanol).

	Found %:	N 4.66; 4.76
$C_{17}H_{26}ClNO$.	Calculated %:	N 4.89

Its nitrile boiled at 125-126° (1.5 mm) and had n_D^{20} 1.4550; d_4^{20} 0.9505; found MR 57.52; calculated MR 57.68

	Found %:	N 7.13; 7.06
$C_{11}H_{20}ClN$.	Calculated %:	N 6.98

13-Chlorotridecanoic Acid. 1,1,1,13-Tetrachlorotridecane boiled at 152-153° (1.5 mm) and had n_D^{20} 1.4842, d_4^{20} 1.1290; found MR 81.63; calculated MR 81.70

	Found %:	C 48.56; 48.69, H 7.28, 7.41; Cl 43.91
$C_{13}H_{24}Cl_4$.	Calculated %:	C 48.47; H 7.45; Cl 44.08

Hydrolysis of the tetrachlorotridecane gave 13-chlorotridecanoic acid in 42% yield. The reaction was accompanied by considerable resinification. 13-Chlorotridecanoic acid melted at 52-53° (from petroleum ether).

Found %: C 62.98; 62.96; H 10.25; 10.16
$C_{13}H_{25}ClO_4$. Calculated %: C 62.83; H 10.05

Its ethyl ester boiled at 147-149° (1.5 mm) and had n_D^{20} 1.4535; d_4^{20} 0.9604; found MR 77.92; calculated MR 77.99

Found %: C 65.18; 65.28; H 10.56; 10.42
$C_{15}H_{29}ClO_4$. Calculated %: C 65.06; H 10.55

Its acid chloride boiled at 146-147° (1.5 mm). Its anilide melted at 70-71° (from methanol).

Found %: N 4.40; 4.43
$C_{21}H_{30}ClNO$. Calculated %: N 4.32

15-Chloropentadecanoic Acid. 1,1,1,15-Tetrachloropentadecane boiled at 176-178° (1 mm) and had n_D^{23} 1.4858; d_4^{20} 1.1078; found MR 90.75; calculated MR 90.94

Found %: C 51.30; 51.26; H 7.77; 7.60
$C_{15}H_{28}Cl_4$. Calculated %: C 51.43; H 8.00

Hydrolysis of the tetrachloropentadecane gave 15-chloropentadecanoic acid in 24% yield. It melted at 62-63° (from petroleum ether).

Found %: C 65.03; 65.22; H 10.63; 10.75
$C_{15}H_{29}ClO_2$. Calculated %: C 65.13; H 10.49

Its ethyl ester boiled at 168-170° (1.5 mm) and melted at 31.5-32.5° (from petroleum ether).

Found %: C 66.83; 66.88; H 10.98; 10.82
$C_{17}H_{33}ClO_2$. Calculated %: C 66.95; H 10.90

Its acid chloride boiled at 165-166° (1.5 mm) and melted at 30-31° (from petroleum ether). Its anilide melted at 79-80° (from methanol).

Found %: N 4.08; 4.06
$C_{23}H_{34}ClNO$. Calculated %: N 3.98

Ethyl 5-Ethoxyvalerate. A mixture of 50 g of ethyl 5-chlorovalerate and sodium ethoxide (prepared from 7.7 g of sodium and 90 ml of absolute alcohol) was heated for five hours. The alcohol was distilled off, water was added to the residue, and the oil that separated was extracted with benzene. Distillation of the reaction products yielded a small amount of the ethyl ester of 4-pentenoic acid and 42.1 g of ethyl 5-ethoxyvalerate, b.p. 87-88° (10 mm); n_D^{20} 1.4225; d_4^{20} 0.9386; found MR 47.16; calculated MR 47.06.

Found %: C 62.15; 62.24; H 10.48; 10.51
$C_9H_{18}O_3$. Calculated %: C 62.07; H 10.34

Ethyl 7-Ethoxyheptanoate. Heating of 48 g of ethyl 7-chloroheptanoate with sodium ethoxide (obtained from 6.3 g of sodium and 80 ml of absolute ethanol) for five hours yielded 45.3 g of ethyl 7-ethoxyheptanoate, b.p. 77-78° (1.5 mm); n_D^{20} 1.4292; d_4^{20} 0.9290; found MR 56.36; calculated MR 56.20.

Found %: C 65.21; 65.18; H 10.81; 10.96
$C_{11}H_{22}O_3$. Calculated %: C 65.34; H 10.89

Triethyl 1,1,5-Pentanetricarboxylate. A mixture of 45 g of ethyl 5-chlorovalerate, sodiomalonic ester (obtained from 70 g of malonic ester and 7.5 g of sodium), 10 g of sodium iodide, and 90 ml of absolute alcohol was heated for six hours. The alcohol was distilled off, water was added to the residue, and the oil that separated was extracted with benzene. Vacuum distillation yielded 67 g (87%) of triethyl 1,1,5-pentanetricarboxylate, b.p. 147-149° (2 mm); n_D^{20} 1.4389; d_4^{20} 1.0568; found MR 71.65; calculated MR 71.81.

Found %: C 58.48; 58.53; H 8.17; 8.22
$C_{14}H_{24}O_6$ Calculated %: C 58.33; H 8.33

A mixture of 60 g of the tricarboxylic ester and 400 ml of hydrochloric acid (1:1) was boiled for four hours. The hydrochloric acid was distilled off under reduced pressure, and the residue was heated at 180-190° until evolution of carbon dioxide ceased (30 minutes). The product was 31.2 g of pimelic acid, m.p. 103-104°.

Triethyl 1,1,7-Heptanetricarboxylate. A mixture of 20 g of ethyl 7-chloroheptanoate, sodiomalonic ester (obtained from 32 g of malonic ester and 2.6 g of sodium), 5 g of sodium iodide, and 50 ml of absolute alcohol was

heated for ten hours. The product was 25.2 g (79%) of triethyl 1,1,7-heptanetricarboxylate, b.p. 169-170° (1.5 mm); n_D^{28} 1.4419; d_4^{28} 1.0316; found MR 81.03; calculated MR 81.04.

	Found %:	C 60.92; 60.98; H 8.89; 8.83
$C_{16}H_{28}O_6$	Calculated %:	C 60.76 H 8.86

Hydrolysis of the tricarboxylic ester with diluted hydrochloric acid gave azelaic acid in good yield.

9-Phenoxynonanoic Acid. A solution of 10 g of 9-chlorononanoic acid, 10 g of phenol, and 7 g of caustic soda in 40 ml of water was refluxed for three hours. The solution was cooled, filtered, and acidified with hydrochloric acid. The precipitate that formed was filtered off and washed carefully with water. The product was 11.8 g (91%) of 9-phenoxynonanoic acid, m.p. 69-70° (from aqueous methanol).

	Found %:	C 72.15; 72.18; H 8.98; 8.79
$C_{15}H_{22}O_3$	Calculated %:	C 72.00 H 8.80

7-Phenoxyheptanoic Acid. A solution of 10 g of 7-chloroheptanoic acid, 11.5 g of phenol, and 7.2 g of caustic soda in 40 ml of water was heated for five hours. The product was 10.2 g of 7-phenoxyheptanoic acid, m.p. 56-57°

5-Phenoxyvaleric Acid. A mixture of 20 g of δ-valerolactone and sodium phenoxide prepared from 20 g of phenol was heated at 200-210° for 4 hours 30 minutes. The melt was cooled and dissolved in water, and the resulting solution was acidified with hydrochloric acid. The precipitate that formed was filtered off and washed with water. The product was 29.5 g (81%) of 5-phenoxyvaleric acid, m.p. 65-66°;

5-(Phenylthio)valeric Acid. A solution of 10 g of 5-chlorovaleric acid and 3 g of caustic soda in 10 ml of water was mixed with a solution of 10 g of benzenethiol and 3.8 g of caustic soda in 15 ml of water; heat was evolved when the solutions were mixed. The mixture was boiled for two hours, cooled, and acidified with hydrochloric acid. Benzenethiol was steam-distilled off. The product was 10.2 g (65%) of 5-(phenylthio)valeric acid, m.p. 63-64° (from benzene-ligroin) (the literature [12] gives 57°).

	Found %:	C 62.76; 62.57; H 6.34; 6.31; S 15.04; 15.10
$C_{11}H_{14}O_2S$	Calculated %:	C 62.80 H 6.56 S 15.21

7-Cyanoheptanoic Acid. A solution was prepared from 16.5 g of 7-chloroheptanoic acid, 4 g of caustic soda, and 30 ml of water. A solution of 8 g of sodium cyanide in 20 ml of water was added, and the mixture was heated at 95-100° for 90 minutes. When the mixture was cool, hydrochloric acid was added, and the oil that separated was extracted with benzene. Vacuum distillation yielded 9.8 g (63%) of 7-cyanoheptanoic acid, b.p. 145-147° (1.5 mm) and m.p. 39-40° (from a mixture of petroleum ether and benzene).

	Found %:	N 9.09; 9.06
$C_8H_{13}NO_2$	Calculated %:	N 9.05

8-Aminooctanoic Acid. 7-Cyanoheptanoic acid (10 g) was dissolved in 30 ml of 25% ammonia and hydrogenated at 65-70° and 90 atm in presence of Raney nickel for two hours. The solution was filtered from the catalyst and evaporated down to remove ammonia. It was then diluted to 50 ml with water, and hydrogen sulfide was passed in order to precipitate nickel. Nickel sulfide was filtered off, and the filtrate was decolorized by treatment with charcoal at the boil. It was evaporated down on a water bath until crystallization began, and ethanol was then added. The mixture was cooled, and the precipitate that formed was filtered off and washed with alcohol. The product was 9.2 g of 8-aminooctanoic acid, m.p. 187-188° (from water) (the literature [13] gives 172°).

	Found %:	N 8.71; 8.70
$C_8H_{17}NO_2$	Calculated %:	N 8.81

7-Hydroxyheptanoic Acid. A solution of 82 g of 7-chloroheptanoic acid and 21 g of caustic soda in 150 ml of water was mixed with a solution of 53 g of sodium carbonate in 250 ml of water. The solution was heated for three hours in an autoclave at 140-150°, cooled, and filtered from insoluble material (4 g, probably polymer of 7-hydroxyheptanoic acid, since it yielded 7-hydroxyheptanoic acid when heated with alkali). It was then acidified with the calculated amount of dilute sulfuric acid. The oil that separated was extracted with ether, and the ether extract was dried with magnesium sulfate. Removal of ether yielded 62.3 g of 7-hydroxyheptanoic acid in the form of a sirup. Oxidation of this substance with nitric acid (sp. gr. 1.40-1.42) resulted in the formation of pimelic acid in good yield.

6-Heptenoic Acid. A solution of 18 g of 7-chloroheptanoic acid, 13.5 g of caustic soda, and 23 g of trimethylamine hydrochloride in 100 ml of water was heated for three hours at 130-140° in an autoclave. The solution was evaporated down to three-quarters of its original volume, 28 g of caustic soda was added, and the mixture was heated

in a copper dish with stirring, first at 130-140°, and then at 160-185°, until evolution of trimethylamine ceased (one hour). From time to time small amounts of water were added to replace loss by evaporation. The hot mixture was diluted with water, cooled, and acidified with dilute sulfuric acid. The oil that separated was extracted with ether, and the extract was dried with calcium chloride. Vacuum distillation yielded 10.1 g of 6-heptenoic acid, b.p. 118-120° (14 mm), n_D^{20} 1.4400; and d_4^{20} 0.9500. Its p-toluidide melted at 60-61°. Data in the literature: 6-heptenoic acid n_D^{17} 1.4425 and d_4^{17} 0.952; p-toluidide m.p. 59.6° [14]. Its amide melted at 83-84° (from water).

	Found %:	N 9.15; 9.21
$C_7H_{13}NO$.	Calculated %:	N 9.06

5-Chlorovalerophenone. Aluminum chloride (28 g) was added gradually with cooling to a solution of 31 g of 5-chlorovaleryl chloride in 40 ml of benzene. There was rise in temperature, hydrogen chloride was evolved, and the aluminum chloride dissolved. When the whole of the aluminum chloride had been added, the solution was set aside for one hour. It was then boiled for five minutes, cooled, and poured onto ice. The benzene layer was separated and washed with water. After removal of solvent the residue crystallized out. The product was 35.4 g (90%) of 5-chlorovalerophenone, m.p. 49-50° (from alcohol) (the literature [15] gives 51°).

7-Chloroheptanophenone. Aluminum chloride (8.3 g) was added gradually with cooling to a solution of 11 g of 7-chloroheptanoyl chloride in 12 ml of benzene. The mixture was set aside for one hour and then poured onto ice. The product was 9.5 g (72%) of 7-chloroheptanophenone, b.p. 147-148° (1.5 mm) and m.p. 34-35° (from methanol).

	Found %:	C 69.32; 69.29; H 7.68; 7.52
$C_{13}H_{17}ClO$.	Calculated %:	C 69.48; H 7.57

Its 2,4-dinitrophenylhydrazone melted at 110-111° (from acetic acid).

	Found %:	N 12.82; 12.86
$C_{21}H_{25}ClN_4O_4$.	Calculated %:	N 12.94

5-Phenylvaleric Acid. Aluminum chloride (28 g) was added gradually to a solution of 25 g of 5-chlorovaleric acid in 75 ml of benzene. The solution was heated for one hour in a water bath, cooled, and poured into a mixture of ice and hydrochloric acid. The benzene solution was washed with water and dried with calcium chloride. The residue remaining after removal of solvent was vacuum-distilled, and yielded 26.5 g (80%) of 5-phenylvaleric acid, b.p. 132-133° (1.5 mm) and m.p. 59-60°.

When 20 g of 5-chlorovaleric acid reacted with 65 ml of benzene in presence of 40 g of aluminum chloride under similar conditions, the products were 14.1 g of 5-phenylvaleric acid and 5.5 g of 1-benzosuberanone, b.p. 124-125° (7 mm), n_D^{20} 1.5618; d_4^{20} 1.0780. The dinitrophenylhydrazone melted at 171-172°.

"Phenylheptanoic Acid". Aluminum chloride (18 g) was added gradually to a solution of 20 g of 7-chloroheptanoic acid in 70 ml of benzene. After being heated for 35 minutes, the solution was cooled and poured into a mixture of ice and hydrochloric acid. The benzene solution was washed with water and dried with calcium chloride. The product was 19.1 g (76.5%) of "phenylheptanoic acid", b.p. 165-166° (3 mm); n_D^{20} 1.5089; d_4^{20} 1.0296; found MR 60.26; calculated MR 60.17.

	Found %:	C 75.56; 75.52; H 8.91; 8.86
$C_{13}H_{18}O_2$.	Calculated %:	C 75.72; H 8.73

Its amide melted at 55.5-56.5° (from a mixture of ether and petroleum ether). For the amide of 7-phenylheptanoic acid the literature [8] gives m.p. 89°.

	Found %:	N 6.68; 6.76
$C_{13}H_{19}NO$.	Calculated %:	N 6.83

When the "phenylheptanoic acid" was oxidized with chromic anhydride, as described below for "phenylnonanoic acid", acetophenone was obtained.

"Phenylnonanoic Acid". Aluminum chloride (16 g) was added to a solution of 20 g of 9-chlorononanoic acid in 70 ml of benzene, and the resulting solution was heated for 45 minutes in a water bath. The product was 18.3 g of "phenylnonanoic acid", b.p. 155-157° (1 mm); n_D^{20} 1.5043; d_4^{20} 0.9957; found MR 69.62; calculated MR 69.40. For 9-phenylnonanoic acid the literature [9] gives m.p. 29-30°, b.p. 215° (12 mm).

	Found %:	C 76.84; 76.78; H 9.32; 9.24
$C_{15}H_{22}O_2$.	Calculated %:	C 76.92; H 9.40

A solution of 12 g of chromic anhydride in 30 ml of glacial acetic acid and 5 ml of water was added to a cooled solution of 10 g of the "phenylnonanoic acid" in 36 ml of glacial acetic acid. The mixture was set aside at room

temperature for several days, and was then diluted with water and extracted with chloroform. The extract was dried with magnesium sulfate. Vacuum distillation yielded about 1.2 g of a low-boiling fraction and 4.1 g of unchanged "phenylnonanoic acid". Treatment of the low-boiling fraction with 2,4-dinitrophenylhydrazine yielded the 2,4-dinitrophenylhydrazone of acetophenone, m.p. 237-238° (from acetic acid) (in admixture with an authentic sample it melted at 237-238°). Also, by treatment with hydroxylamine, acetophenone oxime was obtained, m.p. 58-59° (in admixture with an authentic sample it melted at 58-59°).

"Phenylundecanoic Acid". A mixture of 11 g of 11-chloroundecanoic acid, 60 ml of benzene, and 7.5 g of aluminum chloride yielded 7.9 g of "phenylundecanoic acid", b.p. 186-188° (3 mm); n_D^{20} 1.5005; d_4^{20} 0.9779; found MR 78.87; calculated MR 78.65.

	Found %:	C 77.93; 78.02; H 9.94; 9.94
$C_{17}H_{26}O_2$.	Calculated %:	C 77.92 H 9.93

SUMMARY

1. 11-Chlorodecanoic, 13-chlorotridecanoic, and 15-chloropentadecanoic acids have been prepared by hydrolysis of the corresponding $\alpha,\alpha,\alpha,\omega$-tetrachloroalkanes.

2. The reactivities of some ω-chloro carboxylic acids have been studied.

3. It has been shown that the condensation of 5-chlorovaleric acid with benzene in presence of aluminum chloride proceeds without isomerization, but that isomerization occurs in the corresponding condensations of 7-chloroheptanoic, 9-chlorononanoic, and 11-chloroundecanoic acids.

4. In order to characterize the ω-chloro carboxylic acids studied, some of their derivatives have been prepared.

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CHLORINATION AND DEHYDROCHLORINATION OF POLYCHLORO COMPOUNDS CONTAINING REACTIVE GROUPS

R. Kh. Freidlina, V. N. Kost, and A. N. Nesmeyanov

The reaction of chlorine with unsaturated hydrocarbons is a very complex process. Chlorination of olefins may proceed, depending on conditions, by a heterolytic (eletrophilic), or by a homolytic mechanism. Initial and final reaction components, for example those of structure $CH_2=\overset{|}{C}-\overset{|}{C}-H$ and $CH_2=\overset{|}{C}-\overset{|}{C}-Cl$, readily undergo isomerization, and the compounds formed initially may react further with chlorine and with hydrogen chloride. Reaction may proceed, therefore, in various directions, and among the most important of these are the formation of saturated addition products and the formation of unsaturated chloro olefins by "allyl chlorination". By "allyl chlorination" we mean replacement of hydrogen attached to a carbon atom adjacent to a double bond, the position of the entering chlorine atom being determined by the mechanism of the reaction.

Branched unsaturated hydrocarbons having a tertiary carbon at the double bond react with chlorine even at room temperature with formation of chloro olefins, as was noted for the first time by Lvov and Sheshukov [1]. This important reaction was subsequently investigated by several Russian workers, including Kondakov, Pogorzhelsky, Ostromyslensky, and Tishchenko.

Normal olefins behave differently. At low temperatures they unite with chlorine at the double bond, and at high temperatures (300-600° for propene) they undergo allyl chlorination with formation of chloro olefins [2]. For 1,2-disubstituted ethylenes cases are known in which reaction with chlorine at slightly above room temperature results in the formation of small amounts of chloro olefins, as well as addition products. For example, when chlorine reacted with 2-pentene in a hot carbon tetrachloride medium, a small amount of 1-chloro-2-pentene was isolated, as well as the addition product [3].

This paper describes a study of the reaction of chlorine with compounds containing the 2,2-dichlorovinyl group (or substituted 2,2-dichlorovinyl group) and also the dehydrochlorination of the resulting polychloro compounds. Since compounds of structure $CCl_2=\overset{|}{C}-\overset{|}{C}-Cl$, unlike those of structure $CH_2=\overset{|}{C}-\overset{|}{C}-Cl$, are inert to anionotropic allyl rearrangement [4], it may be expected that the analysis of their behavior in chlorination will be rather simpler.

We have studied the action of chlorine on compounds of structure:

$$CCl_2=CX-CH_2Y,$$

(X = H, Cl; Y = C_6H_5, OCH_3, $N(C_2H_5)_2$, NO_2.

In these compounds the readiness with which the allyl hydrogen atoms are replaced by chlorine should depend on the nature of the substituent attached to the methylene group. The chlorination was carried out under mild conditions in carbon tetrachloride, usually with cooling. For the less reactive substances heating was applied and the reaction mixture was illuminated with a 150-watt filament lamp.

The compounds can be divided into two groups, according to their behavior towards chlorine. The first group includes:

$$CCl_2=CH-CH_2C_6H_5,\ CCl_2=CCl-CH_2C_6H_5,\ CCl_2=CH-CH_2-NO_2,$$

to which chlorine adds smoothly according to the equation

$$CCl_2=CXCH_2Y + Cl_2 \longrightarrow CCl_3CXClCH_2Y. \qquad (1)$$

In these cases the evolution of hydrogen chloride, which is associated with the occurrence of allyl chlorination, does not occur to an appreciable extent. The authors of this paper in collaboration with Zakharkin [5] have shown that compounds of structure $CCl_2=CH-CH_2-CN$ and $CCl_2=CH-CH_2-COOH$ also unite readily with chlorine without yielding appreciable amounts of products of allyl chlorination.

The second group includes compounds of structure:

$$CCl_2=CH-CH_2OCH_3,\ CCl_2=CCl-CH_2OCH_3,\ CCl_2=CHCH_2N(C_2H_5)_2.$$

and even under the mildest conditions at -5° to 0° without irradiation these compounds react with chlorine with copious evolution of hydrogen chloride, indicating the occurrence of allyl chlorination. The main reaction is

$$CCl_2=CX-CH_2Y + 2Cl_2 \longrightarrow CCl_3CXClCHClY + HCl, \qquad (2)$$

These results show that in compounds of structure $CCl_2=CX-CH_2Y$, in which the methylene group is attached to an electron-accepting substituent, the replacement of hydrogen by chlorine is difficult, whereas in the compounds in which the methylene group is attached to an electron-donating substituent, the replacement of hydrogen by chlorine is facilitated. This conclusion is confirmed by the fact that when compounds of the second group react with chlorine in a hydrochloric acid medium allyl chlorination (Equation 2) begins to play a subordinate role and the reaction proceeds mainly according to Equation 1. This effect is clearly associated with the conversion of the electron-donating group into an electron acceptor under these conditions, as indicated in the schemes:

$$CCl_2=CX-CH_2OCH_3 + HCl \rightleftharpoons [CCl_2=CH-CH_2\overset{+}{\underset{H}{O}}-CH_3]Cl'$$

$$CCl_2=CH-CH_2N(C_2H_5)_2 + HCl \rightleftharpoons [CCl_2=CH-CH_2\overset{+}{N}H(C_2H_5)_2]Cl'.$$

It is known also that diallyl ether [6], allyl alcohol, allyl acetate, and allyl benzoate [7] unite smoothly with chlorine in a hydrochloric acid medium.

The tetrachloro compounds that we obtained, namely

$$CCl_2CHClCH_2Y \ [Y=C_6H_5, OCH_3, N(C_2H_5)_2]$$

were subjected to dehydrochlorination with alcoholic potash with the object of determining the effect of the nature of the substituent attached to the methylene group on the direction in which hydrogen chloride was eliminated from these molecules.

In all of these cases elimination was in accord with Zaitsev's rule, i.e.

$$CCl_3-CHCl-CH_2Y \xrightarrow{KOH} CCl_2=CCl-CH_2Y.$$

We have previously shown, in collaboration with Zakharkin [5], that the dehydrochlorination of compounds of structure $CCl_2CHClCH_2CN$ and $CCl_2CHClCH_2COOH$ in presence of alcoholic potash proceeds in the direction contrary to Zaitsev's rule, i.e.

$$CCl_3-CHCl-CH_2Y \xrightarrow{KOH} CCl_2-CH=CHY.$$

The observations now described show that in the dehydrochlorination of compounds of structure $CCl_3-CHCl-CH_2Y$ reaction is in accord with Zaitsev's rule when Y is an electron donor, but when it is a strong electron acceptor the reaction is contrary to Zaitsev's rule.

The phenyl group was found to have opposite effects in the chlorination and dehydrochlorination reactions.

The methods of preparing the compounds studied and of establishing their structures will be clear from the following schemes.

For substances containing the phenyl group:

$$\underset{(I)}{CCl_2=CH-CH_2C_6H_5} \xrightarrow{Cl_2} \underset{(II)}{CCl_3CHClCH_2C_6H_5} \xrightarrow{KOH}$$

$$\longrightarrow \underset{(III)}{CCl_2=CCl-CH_2C_6H_5} \xrightarrow{Cl_2} \underset{(IV)}{CCl_3CCl_2CH_2C_6H_5}.$$

Compound (I) was prepared as already described [4]. Compound (IV) was identified with (2,2,3,3,3-pentachloropropyl) benzene as prepared by the reactions

$$CCl_2=CCl-CH_2Cl + C_6H_6 \xrightarrow{AlCl_3} CCl_2=CCl-CH_2C_6H_5 \xrightarrow{Cl_2} CCl_3CCl_2CH_2C_6H_5,$$

by means of a mixture melting point.

For substances containing a methoxyl group:

$$\underset{(V)}{CCl_2=CH-CH_2OCH_3} \xrightarrow[HCl]{Cl_2} \underset{(VI)}{CCl_2ClCHClCH_2OCH_3} \xrightarrow{KOH} \underset{(VII)}{CCl_2=CCl-CH_2OCH_3} \xrightarrow[HCl]{Cl_2} CCl_3CCl_2CH_2OCH_3;$$

compound (V) was prepared as previously described [8]. Compound (VII) was found to have constants identical with those of the substance synthesized by the reaction:

$$CCl_2{=}CClCH_2Cl + CH_3ONa \longrightarrow CCl_2{=}CClCH_2OCH_3.$$

For compounds containing the diethylamino group:

$$CCl_2{=}CH{-}CH_2N(C_2H_5)_2 \xrightarrow[HCl]{Cl_2} CCl_3CHClCH_2N(C_2H_5)_2 \cdot HCl \xrightarrow{KOH} CCl_2{=}CCl{-}CH_2N(C_2H_5)_2 \xrightarrow{HCl}$$

(VIII)

$$\longrightarrow CCl_2{=}CClCH_2N(C_2H_5)_2 \cdot HCl.$$

(IX)

Compound (VIII) was prepared as previously described [8]. Compound (IX) was identified with the substance prepared by the reaction:

$$CCl_2{=}CClCH_2Cl + (C_2H_5)_2NH \longrightarrow CCl_2{=}CClCH_2N(C_2H_5)_2 \cdot HCl,$$

by making a mixture melting point test on hydrochlorides prepared by the two methods.

For compounds containing the nitro group:

$$CCl_2{=}CH{-}CH_2Cl + AgNO_2 \longrightarrow CCl_2{=}CHCH_2NO_2 \xrightarrow{Cl_2} CCl_3CHClCH_2NO_2.$$

The tetrachlorenitropropane prepared by these reactions had constants that differed from those of the substance originally described as 1,1,1,2-tetrachloro-3-nitropropane, which was synthesized by the action of phosphorus pentachloride on 1,1,1-trichloro-3-nitro-2-propanol. It has since been shown [11] that the compound prepared by the latter method is actually 3,3,3-trichloro-1-nitropropene, and our findings are in agreement with this result.

EXPERIMENTAL

Action of Chlorine on (3,3-Dichloroallyl) benzene

Chlorine was passed at 60° through a solution of 45 g of (3,3-dichloroallyl) benzene in 50 ml of carbon tetrachloride until a state of saturation was attained. The solvent was distilled off, and the residue was vacuum-distilled. A fraction boiling at 130-140° (7 mm) was collected. Redistillation yielded 45 g (82%) of (2,3,3,3-tetrachloropropyl)-benzene, b.p. 111-112° (2 mm); n_D^{18} 1.5535; d_4^{15} 1.3867; found MR 59.58; calculated for $C_9H_8Cl_4$ MR 59.63.

	Found %:	C 42.43; 42.36; H 3.18; 3.20
$C_9H_8Cl_4$.	Calculated %:	C 41.90; H 3.12

Dehydrochlorination of (2,3,3,3-Tetrachloropropyl)benzene

A solution of 10 g (0.18 mole) of caustic potash in 50 ml of alcohol was added dropwise to a stirred solution of 38 g (0.17 mole) of (2,3,3,3-tetrachloropropyl)benzene. The mixture was left overnight at room temperature. The reaction product was precipitated with water, separated, washed, and dried over calcium chloride. Distillation yielded 25 g (80%) of (2,3,3-trichloroallyl)benzene, b.p. 121-122° (8 mm); n_D^{19} 1.5622; d_4^{19} 1.3230; found MR 54.34; calculated for $C_9H_7Cl_3$ MR 54.29. The constants given in the paper of Nesmeyanov, Freidlina, and Firstov [4] were b.p. 121-122° (8 mm); n_D^{20} 1.5630; d_4^{20} 1.3232.

By the action of chlorine on this compound a good yield of crystalline (2,2,3,3,3-pentachloropropyl)benzene, m.p. 76-77°, was obtained.

	Found %:	C 37.11; 37.13; H 2.42; 2.54
$C_9H_7Cl_5$.	Calculated %:	C 36.96; H 2.41

This pentachloro compound gave no melting point depression in admixture with the pentachloro compound obtained by the action of chlorine on the (2,3,3-trichloroallyl)benzene obtained by the condensation of benzene with 1,1,2,3-tetrachloropropene [4].

Action of Chlorine on 3,3-Dichloroallyl Methyl Ether

a) Reaction in Chloroform Solution. When the reaction was carried out in chloroform solution at −5° to 0°, copious evolution of hydrogen chloride was observed. A mixture of chlorination products was obtained, and from this a pentachloro compound was isolated in 62% yield. It boiled at 97-98° (5.5 mm) and had n_D^{20} 1.5098; d_4^{20} 1.5740; it has been described previously [8]. No methyl tetrachloropropyl ether was obtained.

b) Reaction in presence of Hydrogen Chloride. A mixture of 23 g (0.15 mole) of 3,3-dichloroallyl methyl ether, 20 ml of diethyl ether, and 15 ml of concentrated hydrochloric acid was saturated with hydrogen chloride at −5°, and chlorine mixed with hydrogen chloride was then passed through the mixture at −5 to 0° until saturation with chlorine was attained. The mixture was diluted with water, and the organic layer was separated, washed with

a 3% solution of sodium carbonate and with water, and dried over calcium chloride. Distillation yielded 19.5 g (61%) of methyl 2,3,3,3-tetrachloropropyl ether b. p. 58.5-59° (4 mm); n_D^{20} 1.4868; d_4^{20} 1.4568; found MR 41.82; calculated for $C_4H_6Cl_4O$ MR 41.78.

	Found %:	C 22.96; 22.94; H 2.89, 2.88; Cl 67.01; 67.27
$C_4H_6Cl_4O$.	Calculated %:	C 22.66; H 2.85; Cl 66.93

Dehydrochlorination of Methyl 2,3,3,3-Tetrachloropropyl Ether

A solution of 4.5 g of caustic potash in 25 ml of methanol was added a little at a time to 14 g of methyl 2,3,3,3-tetrachloropropyl ether. The mixture was set aside overnight. The mixture was diluted with water, and the lower layer was separated, washed with water, dried over calcium chloride. Distillation yielded 10.3 g (90%) of methyl 2,3,3-trichloroallyl ether, b.p. 53-54° (10 mm); n_D^{20} 1.4871; d_4^{20} 1.3782; found MR 36.62; calculated for $C_4H_5Cl_3O$ MR 36.45.

	Found %:	C 27.29; 27.26; H 2.70, 2.61
$C_4H_5Cl_3O$	Calculated %:	C 27.38; H 2.87

The constants of this compound are in good agreement with the constants of methyl 2,3,3-trichloroallyl ether prepared in the following manner: 1,1,2,3-tetrachloropropene (50 g) was heated for eight hours with a solution of sodium methoxide prepared from 7 g of sodium and 80 ml of methanol. The mixture was diluted with water, and the organic layer was separated, washed with water, and dried over calcium chloride. Distillation yielded 36 g (72%) of methyl 2,3,3-trichloroallyl ether boiling at 54° (10 mm) and having n_D^{20} 1.4875; d_4^{20} 1.3794. The same methyl trichloroallyl ether was obtained by the action of sodium methoxide on 2,3,3,3-tetrachloropropene.

Action of Chlorine on Methyl 2,3,3-Trichloroallyl Ether

a) It was found that a chloroform solution of methyl 2,3,3-trichloroallyl ether does not react, or reacts only very slowly, with chlorine at 0°. When the solution is heated or irradiated reaction proceeds with evolution of hydrogen chloride. For example, when chlorine was passed through a solution of 9 g of methyl 2,3,3-trichloroallyl ether in chloroform maintained at −5° to 0° and irradiated by a 100-watt lamp, a mixture of chlorination products was obtained. This boiled at 89-107° (3 mm) and had n_D^{20} 1.5261–1.5309; d_4^{20} 1.6930 – 1.7227.

b) When the reaction was carried out in presence of hydrogen chloride, the main reaction product was a pentachloro compound. A solution of 8 g of methyl 2,3,3-trichloroallyl ether in 15 ml of concentrated hydrochloric acid was saturated with hydrogen chloride at −5°, and at this temperature, under the illumination of a 150-watt lamp, chlorine and hydrogen chloride were passed for five hours. The mixture was then diluted with water, and the reaction product was extracted with chloroform. The chloroform extract was washed with a 3% solution of sodium carbonate and with water, and then dried over calcium chloride. The solvent was distilled off, and vacuum distillation of the residue yielded 6 g (50%) of a methyl pentachloropropyl ether, b.p. 63-64° (2 mm); n_D^{20} 1.5085; d_4^{20} 1.5765; found MR 46.62; calculated for $C_4H_5Cl_5O$ MR 46.65.

	Found %:	C 19.72; 19.82; H 1.87; 2.00
$C_4H_5Cl_5O$.	Calculated %:	C 19.50; H 2.04

In addition some uncharged methyl 2,3,3-trichloroallyl ether and a small amount of high-boiling fractions were isolated.

Action of Chlorine on 3,3-Dichloro-N,N-diethylallylamine Hydrochloride

The reaction was carried out in concentrated hydrochloric acid saturated with hydrogen chloride at 0°. Reaction did not go in the dark (after chlorine had been passed for five hours the original compound was recovered unchanged). When the mixture was irradiated by a 150-watt lamp at 0 - 5°, 10 g of 3,3-dichloro-N,N-diethylallylamine hydrochloride yielded 12 g (85%) of 2,3,3,3-tetrachloro-N,N-diethylpropylamine hydrochloride, m.p. 180-181° (from absolute alcohol).

	Found %:	C 29.16; 29.07; H 4.94; 4.87
$C_7H_{14}Cl_5N$.	Calculated %:	C 29.04; H 4.87

When the reaction between chlorine and the free base [$CCl_2=CH-CH_2N(C_2H_5)_2$] was carried out in chloroform with cooling, a mixture of hydrochlorides was formed, and these were not investigated further.

Dehydrochlorination of 2,3,3,3-Tetrachloro-N,N-diethylpropylamine

A solution of 1.5 g (0.026 mole) of caustic potash in 10 ml of methanol was added to a solution of 3.5 g (0.012 mole) of 2,3,3,3-tetrachloro-N,N-diethylpropylamine hydrochloride in 10 ml of methanol. The mixture

was left at room temperature overnight, and then diluted with water and extracted with chloroform. The chloroform extract was washed with water and dried over potassium carbonate. The solvent was distilled off, and vacuum distillation of the residue then yielded 1.5 g (60%) of 2,3,3-trichloro-N,N-diethylallylamine, b.p. 81-82° (4 mm); n_D^{20} 1.4894; d_4^{20} 1.1942. The hydrochloride melted at 168-169° (from a mixture of benzene and chloroform). A mixture of this with the hydrochloride of the amine prepared by reaction of 1,1,2,3-tetrachloropropene with diethylamine melted at 168-169°.

Preparation of 2,3,3-Trichloro-N,N-diethylallylamine

A solution of 18 g of 1,1,2,3-tetrachloropropene and 14 g of diethylamine in 40 ml of methanol was heated in a water bath for eight hours. Methanol was distilled off, and the residue was dissolved in dilute hydrochloric acid. The solution was extracted with ether and then made alkaline with 10% caustic potash. The amine that separated was extracted with chloroform, and the chloroform extract was washed with water and dried over potassium carbonate. Distillation yielded 17.8 g (82%) of 2,3,3-trichloro-N,N-diethylallylamine, b.p. 72° (3 mm); n_D^{20} 1.4888; d_4^{20} 1.1922; found MR 52.40; calculated for $C_7H_{12}Cl_3N$ MR 52.60. Its hydrochloride melted at 168-169°.

	Found %:	N 5.45; 5.37
$C_7H_{12}Cl_3N$.	Calculated %:	N 5.53

Preparation of 1,1-Dichloro-3-nitropropene

Silver nitrate (13 g) was added a little at a time to 20 g of 1,1,3-trichloropropene. The mixture was heated in a water bath for one hour. The reaction product was extracted with ether. The ether was distilled off, and vacuum distillation of the residue yielded 3.1 g of 1,1-dichloro-3-nitropropene, b.p. 47-48° (2 mm); n_D^{20} 1.4879; d_4^{20} 1.4491; found MR 31.00; calculated for $C_3H_3Cl_2NO_2$ MR 30.95

	Found %:	C 23.11; 23.32; H 2.16; 2.11
$C_3H_3Cl_2NO_2$.	Calculated %:	C 23.10; H 1.94

Action of Chlorine on 1,1-Dichloro-3-nitropropene

Chlorine was passed for five hours through a boiling solution of 2.3 g of 1,1-dichloro-3-nitropropene that was under the illumination of a 150-watt lamp. The solvent was distilled off, and vacuum distillation of the residue yielded 2.1 g (70%) of a tetrachloronitropropane of boiling point 73-74° (1.5 mm); it had n_D^{20} 1.5005; d_4^{20} 1.6355; found MR 40.84; calculated for $C_3H_3Cl_4NO_2$ MR 41.14.

	Found %:	C 15.72; 15.81; H 1.34; 1.39
$C_3H_3Cl_4NO_2$.	Calculated %:	C 15.88; H 1.33

SUMMARY

1. It has been found that compounds of structure $CCl_2 = CX-CH_2Y$ (X = H, Cl; Y = C_6H_5, OCH_3, $N(C_2H_5)_2$, NO_2) unite smoothly with chlorine at the double bond when the substituent at the methylene group is electron-accepting, but when this substituent is an electron donor allyl chlorination occurs.

2. When the substance of structure $CCl_2 = CX - CH_2Y$ contains an electron-donating substituent at the methylene group (e.g. OCH_3, $N(C_2H_5)_2$) and is capable of being converted into an onium compound in an acid medium, allyl chlorination can be suppressed by carrying out the chlorination in a hydrochloric acid medium.

3. In the dehydrochlorination of compounds of structure $CCl_3CHClCH_2Y$ by means of alcoholic caustic potash, when the substituent is an electron-donating group (e.g. OCH_3, $N(C_2H_5)_2$) the process is in the direction required by Zaitsev's rule, and when it is an electron-accepting group (e.g. CN, COOH) the process is contrary to Zaitsev's rule.

4. In the chlorination of $CCl_2 = CXCH_2C_6H_5$ the effect of the phenyl group is similar to that of the electron-accepting groups. The dehydrochlorination of $CCl_3CHClCH_2C_6H_5$ proceeds in the direction required by Zaitsev's rule.

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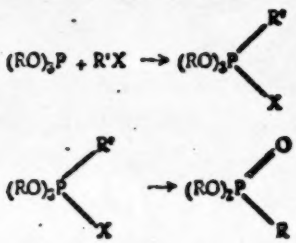
DERIVATIVES OF UNSATURATED PHOSPHONIC ACIDS

COMMUNICATION 5. ESTERS OF 2-ETHOXY-, 2-PROPOXY-, 2-BUTOXY-, AND 2-HEXYLOXY-VINYLPHOSPHONIC ACIDS

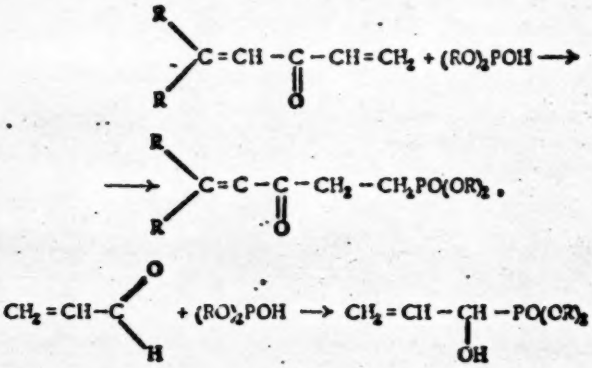
K. N. Anisimov, N. E. Kolobova, and A. N. Nesmeyanov

In our first communication we described a simple, convenient method for the preparation of the previously unknown 2-alkoxyvinylphosphonic dichlorides [1]. Starting from these acid chlorides we have prepared various esters, amides, thio esters, and other derivatives of 2-alkoxyvinylphosphonic acids.

There have been very few investigations on the esters of unsaturated phosphonic acids, and most of these have been carried out by Arbuzov and his students [2 - 10]. They prepared these compounds either with the aid of the Arbuzov isomerization, i.e.,



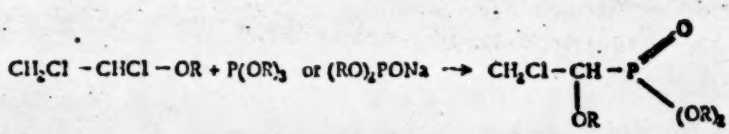
(R' is an unsaturated radical and X is a halogen), or by the addition of dialkyl hydrogen phosphites to unsaturated ketones and aldehydes in presence of sodium alkoxides, i.e.

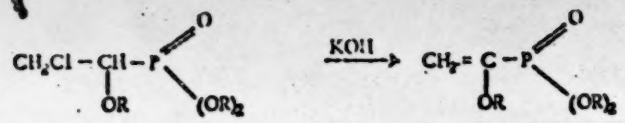


Also, Kabachnik [11] has described the syntheses of the diethyl and bis(2-chloroethyl) esters of vinylphosphonic acid. He obtained these compounds by the elimination of hydrogen chloride from the corresponding esters of 2-chloroethylphosphonic acid with potassium hydroxide solution:

$$Cl-CH_2-CH_2PO(OR)_2 + KOH = CH_2=CHPO(OR)_2 + KCl + H_2O.$$

Pudovik and Denisova [12] have recently described syntheses of the ethyl esters of 1-ethoxy- and 2-butoxyvinylphosphonic acids. The general scheme of the syntheses was as follows:





Diesters of 2-alkoxyvinylphosphonic acids can be prepared by various methods:

1. Reaction of alcohols with 2-alkoxy (or phenoxy) vinylphosphonic dichlorides in presence of pyridine

$$ROCH=CHPOCl_2 + 2ROH + 2C_5H_5N = ROCH=CHPO(OR)_2 + 2C_5H_5N \cdot HCl.$$

2. Reaction of alcohols with these acid chlorides, cooling being applied

$$RO \cdot CH=CHPOCl_2 + 2ROH = ROCH=CHPO(OR)_2 + 2HCl.$$

3. Reaction of the acid chlorides with sodium alkoxides

$$RO \cdot CH=CHPOCl_2 + 2RONa = ROCH=CHPO(OR)_2 + 2NaCl.$$

4. Reaction of salts of 2-alkoxy (or phenoxy) vinylphosphonic acids with alkyl halides

$$RO \cdot CH=CHPO(ONa)_2 + RX = ROCH=CHPO(OR)_2 + 2NaCl.$$

We used the first method, which is due to Milobendzki and Sachnowski [13]. By this means we have prepared the dimethyl, diethyl, dipropyl, diisopropyl, dibutyl, diisobutyl, diallyl, dihexyl, bis(2-methoxyethyl), and bis(2-ethoxyethyl) esters of 2-ethoxy-, 2-propoxy-, 2-butoxy-, and 2-hexyloxy-vinylphosphonic acids. Yields of up to 80% were obtained. All of the esters are liquids that can be vacuum-distilled without decomposition and are readily soluble in the usual organic solvents. When vacuum-distilled, the diisopropyl esters of 2-ethoxy-, 2-propoxy-, 1-butoxy-, and 2-hexyloxy-vinylphosphonic acids underwent partial polymerization with formation of a thick mass in the distillation flask. The yields of these esters were therefore somewhat lower than those of the other esters. The diallyl esters of 2-alkoxyvinylphosphonic acids undergo polymerization, and will copolymerize with unsaturated compounds, in presence of organic peroxides.

The physical constants of the synthesized esters are given in Table 1-4.

EXPERIMENTAL

Diesters of 2-Ethoxyvinylphosphonic Acid

Dimethyl 2-Ethoxyvinylphosphonate $C_2H_5OCH=CHPO(OCH_3)_2$. A mixture of 7.7 g of absolute methanol, 19.7 g of pyridine, and 100 ml of benzene was prepared in a three-necked flask fitted with stirrer, reflux condenser protected with a calcium chloride tube, and dropping funnel. The mixture was well cooled and stirred while addition was made of 23 g of 2-ethoxyvinylphosphonic dichloride diluted with an equal volume of benzene. When the whole of the acid chloride had been added, the reaction mixture was heated for two hours in a water bath. The precipitate was filtered off, and the filtrate was treated three times with a saturated solution of sodium carbonate. It was then dried with calcined potassium carbonate. On the next day the benzene was driven off and the residue was vacuum-distilled. Three fractionations yielded 13 g (56%) of dimethyl 2-ethoxyvinylphosphonate, b.p. 87° (2mm); d_4^{25} 1.1451; n_D^{20} 1.4508

	Found %:	C 39.91; 39.84;	H 7.44; 7.41
$C_6H_{13}O_4P$.	Calculated %:	C 40.00;	H 7.22

All of the other esters were prepared by the above-described method.

Diethyl 2-Ethoxyvinylphosphonate $C_2H_5OCH=CHPO(OC_2H_5)_2$. The product obtained from 15 g of 2-ethoxyvinylphosphonic dichloride, 7.3 g of absolute ethanol, and 13 g of pyridine was 7.5 g (45%) of a substance having b.p. 99.5-100°(2 mm); d_4^{25} 1.0710; n_D^{20} 1.4476

	Found %:	C 46.50; 46.48;	H 8.82; 8.76
$C_8H_{17}O_4P$.	Calculated %:	C 46.15;	H 8.17

Dipropyl 2-Ethoxyvinylphosphonate $C_2H_5OCH=CHPO(OC_3H_7\text{-}n)_2$. 2-Ethoxyvinylphosphonic dichloride (16 g) was added to a solution of 10.15 g of propyl alcohol in 80 ml of benzene, and 14 g (70%) of the ester was isolated. It had b.p. 103°(1.5 mm); d_4^{20} 1.0335; n_D^{20} 1.4475

	Found %:	C 50.90; 50.99;	H 9.09; 9.07
$C_{10}H_{21}O_4P$.	Calculated %:	C 50.84;	H 8.89

TABLE 1

Formula of compound	B.p. in °C (p in mm Hg)	n_D^{20}	d_4^{20}
$C_2H_5-O-CH=CHPO(OCH_3)_2$	87 (2)	1,4508	1,1451
$C_2H_5-O-CH=CHPO(OC_2H_5)_2$	99,5 (2)	1,4476	1,0710
$C_2H_5-O-CH=CHPO(OC_3H_7\text{-}n)_2$	103 (1,5)	1,4475	1,0335
$C_2H_5-O-CH=CHPO(OC_3H_7\text{-}i)_2$	91 (2)	1,4402	1,0171
$C_2H_5-O-CH=CHPO(OC_4H_9\text{-}n)_2$	127 (2)	1,4492	1,0069
$C_2H_5-O-CH=CHPO(OC_4H_9\text{-}i)_2$	107 (0,5)	1,4453	1,0004
$C_2H_5-O-CH=CHPO(OC_5H_5)_2$	112 (1)	1,4698	1,0792
$C_2H_5-O-CH=CHPO(OC_6H_{13}\text{-}n)_2$	157–158 (2)	1,4511	0,9710
$C_2H_5-O-CH=CHPO(OCH_2-CH_2-OCH_3)_2$	155 (2)	1,4568	1,1267
$C_2H_5-O-CH=CHPO(OCH_2-CH_2-OC_2H_5)_2$	158 (1)	1,4545	1,0842

TABLE 2

Formula of compound	B.p. in °C (p in mm Hg)	n_D^{20}	d_4^{20}
$n\text{-}C_3H_7-O-CH=CHPO(OCH_3)_2$	95 (1)	1,4500	1,1095
$n\text{-}C_3H_7-O-CH=CHPO(OC_2H_5)_2$	106 (1)	1,4455	1,0523
$n\text{-}C_3H_7-O-CH=CHPO(OC_3H_7\text{-}n)_2$	128 (2)	1,4471	1,0201
$n\text{-}C_3H_7-O-CH=CHPO(OC_3H_7\text{-}i)_2$	110 (2)	1,4402	1,0042
$n\text{-}C_3H_7-O-CH=CHPO(OC_4H_9\text{-}n)_2$	139 (2)	1,4485	0,9969
$n\text{-}C_3H_7-O-CH=CHPO(OC_4H_9\text{-}i)_2$	121 (2)	1,4449	0,9906
$n\text{-}C_3H_7-O-CH=CHPO(OC_5H_5)_2$	123 (1)	1,4675	1,0557
$n\text{-}C_3H_7-O-CH=CHPO(OC_6H_{13}\text{-}n)_2$	157 (1)	1,4509	0,9664
$n\text{-}C_3H_7-O-CH=CHPO(OCH_2-CH_2-OCH_3)_2$	158 (1)	1,4565	1,1089
$n\text{-}C_3H_7-O-CH=CHPO(OCH_2-CH_2-OC_2H_5)_2$	156 (2)	1,4580	1,0694

TABLE 3

Formula of compound	B.p. in °C (p in mm Hg)	n_D^{20}	d_4^{20}
$n\text{-}C_4H_9-O-CH=CHPO(OCH_3)_2$	111 (2)	1,4515	1,0867
$n\text{-}C_4H_9-O-CH=CHPO(OC_2H_5)_2$	116 (2)	1,4460	1,0360
$n\text{-}C_4H_9-O-CH=CHPO(OC_3H_7\text{-}n)_2$	123 (2)	1,4478	1,0060
$n\text{-}C_4H_9-O-CH=CHPO(OC_3H_7\text{-}i)_2$	105 (2)	1,4401	0,9916
$n\text{-}C_4H_9-O-CH=CHPO(OC_4H_9\text{-}n)_2$	144 (2)	1,4491	0,9879
$n\text{-}C_4H_9-O-CH=CHPO(OC_4H_9\text{-}i)_2$	131,5 (2)	1,4460	0,9810
$n\text{-}C_4H_9-O-CH=CHPO(OC_5H_5)_2$	139,5 (2)	1,4651	1,0442
$n\text{-}C_4H_9-O-CH=CHPO(OC_6H_{13}\text{-}n)_2$	164–165 (2)	1,4518	0,9635
$n\text{-}C_4H_9-O-CH=CHPO(OCH_2-CH_2-OCH_3)_2$	161 (2)	1,4558	1,0873
$n\text{-}C_4H_9-O-CH=CHPO(OCH_2-CH_2-OC_2H_5)_2$	164 (2)	1,4532	1,0584

Diisopropyl 2-ethoxyvinylphosphonate $C_2H_5OCH=CHPO(OC_3H_7\text{-}i)_2$. Isopropyl alcohol was substituted for propyl alcohol in the above synthesis, the amounts taken and the reaction conditions being exactly the same. The yield of diisopropyl 2-ethoxyvinylphosphonate was 10 g (50%). It had b.p. 91° (2 mm); d_4^{20} 1.0171; n_D^{20} 1.4402.

Found %: C 51.04; 51.10; H 8.97; 9.10

$C_{10}H_{21}O_4P$. Calculated %: C 50.84; H 8.89

Dibutyl 2-Ethoxyvinylphosphonate $C_2H_5OCH=CHPO(OC_4H_9\text{-}n)_2$. The product obtained from 14 g of butyl alcohol, 15.81 g of pyridine, and 18.9 g of 2-ethoxyvinylphosphonic dichloride was 20 g (75%) of dibutyl 2-ethoxyvinylphosphonate, b.p. 127° (2 mm); d_4^{20} 1.0069; n_D^{20} 1.4492.

Found %: C 54.80; 54.78; H 9.70; 9.49

$C_{12}H_{25}O_4P$. Calculated %: C 54.54; H 9.46

Diisobutyl 2-Ethoxyvinylphosphonate $C_2H_5OCH=CHPO(OC_4H_9\text{-}i)_2$. The product obtained from 14.81 g of isobutyl alcohol, 15.81 g of pyridine, and 18.9 g of 2-ethoxyvinylphosphonic dichloride was 20 g (75%) of the ester, b.p. 107° (0.5 mm); d_4^{20} 1.0004; n_D^{20} 1.4453.

Found %: C 54.72; 54.31; H 9.20; 9.35

$C_{12}H_{25}O_4P$. Calculated %: C 54.54; H 9.46

TABLE 4

Formula of compound	B.p. in °C (p in mm Hg)	n_D^{20}	d_4^{20}
$n\text{-}C_5H_{11}\text{-}O\text{-}CH=CHPO(OCH_3)_2$	125 (2)	1.4530	1.0498
$n\text{-}C_5H_{11}\text{-}O\text{-}CH=CHPO(OC_2H_5)_2$	136 (2)	1.4495	1.0110
$n\text{-}C_5H_{11}\text{-}O\text{-}CH=CHPO(OC_3H_7\text{-}n)_2$	138–139 (2)	1.4500	0.9891
$n\text{-}C_5H_{11}\text{-}O\text{-}CH=CHPO(OC_3H_7\text{-}i)_2$	129 (2)	1.4402	0.9804
$n\text{-}C_5H_{11}\text{-}O\text{-}CH=CHPO(OC_4H_9\text{-}n)_2$	156 (1)	1.4496	0.9723
$n\text{-}C_5H_{11}\text{-}O\text{-}CH=CHPO(OC_4H_9\text{-}i)_2$	151 (1)	1.4475	0.9660
$n\text{-}C_5H_{11}\text{-}O\text{-}CH=CHPO(OC_6H_5)_2$	151 (1)	1.4650	1.0178
$n\text{-}C_5H_{12}\text{-}O\text{-}CH=CHPO(OC_6H_{13}\text{-}n)_2$	190 (2)	1.4528	0.9515
$n\text{-}C_5H_{11}\text{-}O\text{-}CH=CHPO(OCH_2\text{-}CH_2\text{-}OCH_3)_2$	171 (2)	1.4560	1.0632
$n\text{-}C_5H_{11}\text{-}O\text{-}CH=CHPO(OCH_2\text{-}CH_2\text{-}OC_2H_5)_2$	188 (2)	1.4593	1.0348

Diallyl 2-Ethoxyvinylphosphonate $C_2H_5OCH=CHPO(OC_3H_5)_2$. The product obtained from 11.6 g of allyl alcohol, 15.8 g of pyridine, and 18.9 g of 2-ethoxyvinylphosphonic dichloride was 13 g (56%) of the ester, b.p. 112° (1 mm); d_4^{20} 1.0782; n_D^{20} 1.4698.

Found %: C 51.62; 51.38; H 7.28; 7.38

$C_{10}H_{17}O_4P$. Calculated %: C 51.72; H 7.32

Dihexyl 2-Ethoxyvinylphosphonate $C_2H_5OCH=CHPO(OC_6H_{13}\text{-}n)_2$. 2-Ethoxyvinylphosphonic dichloride (9.45 g) was added to 10.21 g of hexyl alcohol and 7.9 g of pyridine, and 9 g of dihexyl 2-ethoxyvinylphosphonate was isolated. It had b.p. 157-158° (2 mm); d_4^{20} 0.9710; n_D^{20} 1.4511

Found %: C 60.40; 60.38; H 10.31; 10.35

$C_{16}H_{33}O_4P$. Calculated %: C 60.00; H 10.31

Bis(2-methoxyethyl) 2-Ethoxyvinylphosphonate $C_2H_5OCH=CHPO(OCH_2\text{-}CH_2\text{-}OCH_3)_2$. The product obtained from 15 g of 2-methoxyethanol, 15.8 g of pyridine, and 18.9 g of 2-ethoxyvinylphosphonic dichloride was 20 g (76%) of a substance of b.p. 155° (2 mm); d_4^{20} 1.1267; n_D^{20} 1.4568.

Found %: P 11.46; 11.45

$C_{10}H_{21}O_6P$. Calculated %: P 11.58

Bis(2-ethoxyethyl) 2-Ethoxyvinylphosphonate $C_2H_5OCH=CHPO(OCH_2\text{-}CH_2\text{-}OC_2H_5)_2$. The product obtained from 18 g of 2-ethoxyethanol, 15.8 g of pyridine, and 18.9 g of 2-ethoxyvinylphosphonic dichloride was 22 g (70%) of a substance of b.p. 158° (1 mm); d_4^{20} 1.0842; n_D^{20} 1.4545

Found %: P 10.47; 10.42

$C_{12}H_{25}O_6P$. Calculated %: P 10.47

Diesters of 2-Propoxyvinylphosphonic Acid

Dimethyl 2-Propoxyvinylphosphonate n-$C_3H_7OCH{=}CHPO(OCH_3)_2$. 2-Propoxyvinylphosphonic dichloride (10.15 g) was added to a mixture of 3.2 g of methanol, 7.9 g of pyridine, and 80 ml of benzene. The substance isolated (6.5 g) had b.p. 95° (1 mm); d_4^{20} 1.1095; n_D^{20} 1.4500.

Found %: P 15.98; 15.76

$C_7H_{15}O_4P$. Calculated %: P 15.97

Diethyl 2-Propoxyvinylphosphonate n-$C_3H_7{-}O{-}CH{=}CHPO(OC_2H_5)_2$. The product obtained from 4.6 g of ethanol, 7.9 g of pyridine, and 10.15 g of 2-propoxyvinylphosphonic dichloride was 7.5 g of a substance of b.p. 106° (1 mm) d_4^{20} 1.0523; n_D^{20} 1.4455.

Found %: P 13.92; 13.98

$C_9H_{19}O_4P$. Calculated %: P 13.96

Dipropyl 2-Propoxyvinylphosphonate n-$C_3H_7OCH{=}CHPO(OC_3H_7\text{-}n)_2$. 2-Propoxyvinylphosphonic dichloride (10.15 g) was added to 6 g of propyl alcohol and 8 g of pyridine, and 7.3 g (60%) of dipropyl 2-propoxyvinylphosphonate was isolated. It had b.p. 128° (2 mm); d_4^{20} 1.0201; n_D^{20} 1.4471.

Found %: P 12.36; 12.29

$C_{11}H_{23}O_4P$. Calculated %: P 12.40

Diisopropyl 2-Propoxyvinylphosphonate n-$C_3H_7OCH{=}CHPO(OC_3H_7\text{-}i)_2$. 2-Propoxyvinylphosphonic dichloride (10.15 g) was added to 6 g of isopropyl alcohol and 8 g of pyridine, and the product was 7.2 g of a substance of b.p. 110° (2 mm); d_4^{20} 1.0042; n_D^{20} 1.4402.

Found %: P 12.33; 12.29

$C_{11}H_{23}O_4P$. Calculated %: P 12.40

Dibutyl 2-Propoxyvinylphosphonate n-$C_3H_7OCH{=}CHPO(OC_4H_9\text{-}n)_2$. The product obtained from 7.4 g of butyl alcohol, 8 g of pyridine, and 10.15 g of 2-propoxyvinylphosphonic dichloride was 8.5 g (64%) of a substance of b.p. 139° (2 mm); d_4^{20} 0.9969 . n_D^{20} 1.4485.

Found %: P 10.99; 11.17

$C_{13}H_{27}O_4P$. Calculated %: P 11.15

Diisobutyl 2-Propoxyvinylphosphonate n-$C_3H_7OCH{=}CHPO(OC_4H_9\text{-}i)_2$. Isobutyl alcohol was substituted for butyl alcohol in the above synthesis, the amounts taken and the reaction conditions being exactly the same. The product (9.7 g) had b.p. 121° (2 mm); d_4^{20} 0.9906; n_D^{20} 1.4449.

Found %: C 55.77; 55.72; H 9.82; 9.72; P 11.23; 11.22;

$C_{13}H_{27}O_4P$. Calculated %: C 56.11; H 9.71; P 11.15

Diallyl 2-Propoxyvinylphosphonate n-$C_3H_7OCH{=}CHPO(OC_3H_5)_2$. The product obtained from 5.8 g of allyl alcohol, 8 g of pyridine, and 10.15 g of 2-propoxyvinylphosphonic dichloride was 7 g of diallyl 2-propoxyvinylphosphonate, b.p. 123° (1 mm); d_4^{20} 1.0557; n_D^{20} 1.4675.

Found %: C 55.63; 53.53; H 7.79; 7.88

$C_{11}H_{19}O_4P$. Calculated %: C 53.65; H 7.72

Dihexyl 2-Propoxyvinylphosphonate n-$C_3H_7OCH{=}CHPO(OC_6H_{13}\text{-}n)_2$. 2-Propoxyvinylphosphonic dichloride (10.15g) was added to 10.21 g of hexyl alcohol and 7.8 g of pyridine. The product (9.5 g) had b.p. 157° (1 mm); d_4^{20} 0.9664; n_D^{20} 1.4509.

Found %: P 8.96; 9.13

$C_{17}H_{35}O_4P$. Calculated %: P 9.25

Bis(2-methoxyethyl) 2-Propoxyvinylphosphonate n-$C_3H_7OCH{=}CHPO(OCH_2{-}CH_2OCH_3)_2$. 2-Propoxyvinylphosphonic dichloride (10.15 g) was added to 7.6 g of 2-methoxyethanol and 7.9 g of pyridine. The product (9 g) had b.p. 158° (1 mm); d_4^{20} 1.1089; n_D^{20} 1.4565.

Found %: C 47.12; 46.93; H 8.35; 8.26

$C_{11}H_{23}O_6P$. Calculated %: C 46.80; H 8.15

Bis(2-ethoxyethyl) 2-Propoxyvinylphosphonate n-$C_3H_7OCH{=}CHPO(OCH_2{-}CH_2OC_2H_5)_2$. The product obtained from 9 g of 2-ethoxyethanol, 7.9 g of pyridine, and 10.15 g of 2-propoxyvinylphosphonic dichloride was 10 g of a sub-

stance of b.p. 160° (1 mm); d_4^{20} 1.0691; n_D^{20} 1.4580.

Found %: C 50.33; 50.40; H 8.78; 8.82

$C_{13}H_{27}O_5P$. Calculated %: C 50.32; H 8.70

Diesters of 2-Butoxyvinylphosphonic Acid

Dimethyl 2-Butoxyvinylphosphonate n-$C_4H_9OCH{=}CHPO(OCH_3)_2$. 2-Butoxyvinylphosphonic dichloride (21.7 g) was added to 6.4 g of methanol and 15.8 g of pyridine. The product was 11 g (51%) of a substance of b.p. 111° (2 mm); d_4^{20} 1.0867; n_D^{20} 1.4515.

Found %: C 46.32; 46.35; H 8.06; 8.00

$C_8H_{17}O_4P$. Calculated %: C 46.15; H 8.17

Diethyl 2-Butoxyvinylphosphonate n-$C_4H_9OCH{=}CHPO(OC_2H_5)_2$. 2-Butoxyvinylphosphonic dichloride (10.85 g) was added to 4.6 g of absolute ethanol and 7.9 g of pyridine. An ester was isolated having b.p. 116.5° (2 mm); d_4^{20} 1.0360; n_D^{20} 1.4460.

Found %: C 50.53; 50.66; H 8.65; 8.80

$C_{16}H_{21}O_4P$. Calculated %: C 50.84; H 8.89

Dipropyl 2-Butoxyvinylphosphonate n-$C_4H_9OCH{=}CHPO(OC_3H_7\text{-}n)_2$. The product obtained from 10.85 g of 2-butoxyvinylphosphonic dichloride, 6 g of propyl alcohol, and 7.9 g of pyridine was 9 g (68%) of a substance of b.p. 123° (2 mm); d_4^{20} 1.0060; n_D^{20} 1.4478.

Found %: C 54.40; 54.48; H 9.34; 9.49

$C_{12}H_{25}O_4P$. Calculated %: C 54.54; H 9.46

Diisopropyl 2-Butoxyvinylphosphonate n-$C_4H_9OCH{=}CHPO(OC_3H_7\text{-}i)_2$. The product obtained from 6 g of isopropyl alcohol, 7.9 g of pyridine, and 10.85 g of 2-butoxyvinylphosphonic dichloride was 5 g of a substance of b.p. 105° (2 mm); d_4^{20} 0.9916; n_D^{20} 1.4401.

Found %: C 54.19; 54.23; H 9.36; 9.46

$C_{12}H_{25}O_4P$. Calculated %: C 54.54; H 9.46

Dibutyl 2-Butoxyvinylphosphonate n-$C_4H_9OCH{=}CHPO(OC_4H_9\text{-}n)_2$. The product obtained from 7.4 g of butyl alcohol, 7.9 g of pyridine, and 10.85 g of 2-butoxyvinylphosphonic dichloride was 9 g (67%) of an ester of b.p. 144° (2 mm); d_4^{20} 0.9879, n_D^{20} 1.4491.

Found %: C 57.87; 57.80; H 9.99; 9.96

$C_{14}H_{29}O_4P$. Calculated %: C 57.53; H 9.93

Diisobutyl 2-Butoxyvinylphosphonate n-$C_4H_9OCH{=}CHPO(OC_4H_9\text{-}i)_2$. 2-Butoxyvinylphosphonic dichloride (10.85 g) was added to 7.4 g of isobutyl alcohol and 7.9 g of pyridine. The product was 8.5 g (63%) of a substance of b.p. 131.5° (2 mm); d_4^{20} 0.9810; n_D^{20} 1.4460.

Found %: C 57.01; 57.06; H 10.16; 10.15

$C_{14}H_{29}O_4P$. Calculated %: C 57.53; H 9.93

Diallyl 2-Butoxyvinylphosphonate n-$C_4H_9OCH{=}CHPO(OC_3H_5)_2$. The product obtained from 10.85 g of 2-butoxyvinylphosphonic dichloride, 5.8 g of allyl alcohol, and 7.9 g of pyridine was 7 g (50%) of an ester of b.p. 139.5° (2 mm) d_4^{20} 1.0442; n_D^{20} 1.4651.

Found %: C 54.88; 55.09; H 8.05; 7.88

$C_{12}H_{21}O_4P$. Calculated %: C 55.38; H 8.07

Dihexyl 2-Butoxyvinylphosphonate n-$C_4H_9OCH{=}CHPO(OC_6H_{13}\text{-}n)_2$. The product obtained from 10.21 g of hexyl alcohol, 7.9 g of pyridine, and 10.85 g of 2-butoxyvinylphosphonic dichloride was 10 g (57%) of a substance of b.p. 164–165° (2 mm); d_4^{20} 0.9635; n_D^{20} 1.4518.

Found %: C 62.13; 61.99; H 10.58; 10.89

$C_{18}H_{37}O_4P$. Calculated %: C 62.06; H 10.63

Bis(2-methoxyethyl) 2-Butoxyvinylphosphonate n-$C_4H_9OCH{=}CHPO(OCH_2{-}CH_2OCH_3)_2$. 2-Butoxyvinylphosphonic dichloride (21.05 g) was added to 14.57 g of 2-methoxyethanol and 15.28 g of pyridine. The product was 16 g (55%) of a substance of b.p. 161° (2 mm); d_4^{20} 1.0873; n_D^{20} 1.4558

Found %: P 10.32; 10.55

$C_{12}H_{25}O_6P$. Calculated %: P 10.47

Bis(2-ethoxyethyl) 2-butoxyvinylphosphonate n-$C_4H_9OCH{=}CHPO(OCH_2{-}CH_2OC_2H_5)_2$. The product obtained from 9 g of 2-ethoxyethanol, 7.9 g of pyridine, and 10.85 g of 2-butoxyvinylphosphonic dichloride was 8 g (50%) of an ester of b.p. 164° (2 mm); d_4^{20} 1.0584; n_D^{20} 1.4532.

Found %: P 9.28; 9.43

$C_{14}H_{29}O_6P$. Calculated %: P 9.56

Diesters of 2-(Hexyloxy)vinylphosphonic Acid.

Dimethyl 2-(Hexyloxy)vinylphosphonate n-$C_6H_{13}OCH{=}CHPO(OCH_3)_2$. The product obtained from 3.2 g of methanol, 7.9 g of pyridine and 12.25 g of 2-(hexyloxy)vinylphosphonic dichloride was 6 g of an ester of b.p. 125° (22 mm); d_4^{20} 1.0498; n_D^{20} 1.4530.

Found %: C 50.68; 50.80; H 8.95; 8.82

$C_{10}H_{21}O_4P$. Calculated %: C 50.84; H 8.89

Diethyl 2-(Hexyloxy)vinylphosphonate n-$C_6H_{13}OCH{=}CHPO(OC_2H_5)_2$. The product obtained from 4.6 g of ethanol, 7.9 g of pyridine, and 12.28 g of 2-(hexyloxy)vinylphosphonic dichloride was 8 g of a substance of b.p. 136° (2 mm); d_4^{20} 1.0110; n_D^{20} 1.4495.

Found %: P 11.68; 11.71

$C_{12}H_{25}O_4P$. Calculated %: P 11.75

Dipropyl 2-(Hexyloxy)vinylphosphonate n-$C_6H_{13}OCH{=}CHPO(OC_3H_7\text{-}n)_2$. 2-(Hexyloxy)vinylphosphonic dichloride (12.25 g) was added to 6 g of propyl alcohol and 7.9 g of pyridine. The product was 11 g of an ester of b.p. 138–139° (1 mm); d_4^{20} 0.9891; n_D^{20} 1.4500.

Found %: P 10.34; 10.57

$C_{14}H_{29}O_4P$. Calculated %: P 10.61

Diisopropyl 2-(Hexyloxy)vinylphosphonate n-$C_6H_{13}OCH{=}CHPO(OC_3H_7\text{-}i)_2$. The product obtained from 6 g of isopropyl alcohol, 7.9 g of pyridine, and 12.25 g of 2-(hexyloxy)vinylphosphonic dichloride was 5 g of a substance of b.p. 129° (1 mm); d_4^{20} 0.9804; n_D^{20} 1.4402.

Found %: P 10.86; 10.87

$C_{14}H_{29}O_4P$. Calculated %: P 10.61

Dibutyl 2-(Hexyloxy)vinylphosphonate n-$C_6H_{13}OCH{=}CHPO(OC_4H_9\text{-}n)_2$. The product obtained from 7.4 g of butyl alcohol, 7.9 g of pyridine and 12.25 g of 2-(hexyloxy)vinylphosphonic dichloride was 12 g of an ester of b.p. 156° (1 mm); d_4^{20} 0.9723; n_D^{20} 1.4496.

Found %: C 60.07; 60.09; H 10.63; 10.62

$C_{16}H_{33}O_4P$. Calculated %: C 60.00; H 10.31

Diisobutyl 2-(Hexyloxy)vinylphosphonate n-$C_6H_{13}OCH{=}CHPO(OC_4H_9\text{-}i)_2$. 2-(Hexyloxy)vinylphosphonic dichloride (12.25 g) was added to 7.4 g of isobutyl alcohol and 7.9 g of pyridine. The product was an ester (9 g) of b.p. 151° (1 mm); d_4^{20} 0.9660; n_D^{20} 1.4475.

Found %: C 60.37; 60.28; H 10.54; 10.55

$C_{16}H_{33}O_4P$. Calculated %: C 60.00; H 10.31

Diallyl 2-(Hexyloxy)vinylphosphonate n-$C_6H_{13}OCH{=}CHPO(OC_3H_5)_2$. The product obtained from 5.8g of allyl alcohol, 7.9 g of pyridine, and 12.25 g of 2-(hexyloxy)vinylphosphonic dichloride was 8 g of a substance, b.p. 151° (1 mm). d_4^{20} 1.0178; n_D^{20} 1.4650.

Found %: C 58.07; 58.16; H 8.60; 8.78

$C_{14}H_{25}O_4P$. Calculated %: C 58.33; H 8.68

Dihexyl 2-(Hexyloxy)vinylphosphonate n-$C_6H_{13}OCH{=}CHPO(OC_6H_{13}\text{-}n)_2$. The product obtained from 10.21 g of hexyl alcohol, 7.9 g of pyridine, and 12.21 g of 2-(hexyloxy)vinylphosphonic dichloride was an ester (11 g) of b.p. 190° (2 mm); d_4^{20} 0.9515; n_D^{20} 1.4528.

Found %: C 64.00; 63.79; H 10.93; 11.16

$C_{20}H_{41}O_4P$. Calculated %: C 63.82; H 10.90

Bis(2-methoxyethyl) 2-(Hexyloxy)vinylphosphonate $n\text{-}C_6H_{13}OCH{=}CHPO(OCH_2{-}CH_2{-}OCH_3)_2$. The product obtained from 7.6 g of 2-methoxyethanol and 12.25 g of 2-(hexyloxy)vinylphosphonic dichloride in presence of 7.9 g of pyridine was 7.4 g of a substance of b.p. 171° (1 mm); d_4^{20} 1.0632; n_D^{20} 1.4560.

Found %: P 9.56; 9.42

$C_{16}H_{29}O_6P$. Calculated %: P 9.56

Bis (2-ethoxyethyl) 2-(Hexyloxy)vinylphosphonate $n\text{-}C_6H_{13}OCH{=}CHPO(OCH_2{-}CH_2OC_2H_5)_2$. 2-(Hexyloxy)vinylphosphonic dichloride (12.25 g) was added to 9 g of 2-ethoxyethanol and 7.9 g of pyridine. The product was an ester (8 g) of b.p. 188° (1 mm); d_4^{20} 1.0348; n_D^{20} 1.4593.

Found %: C 54.39; 54.31; H 9.56; 9.58

$C_{16}H_{33}O_6P$. Calculated %: C 54.54; H 9.37

SUMMARY

1. Diesters of 2-ethoxy-, 2-propoxy-, 2-butoxy-, and 2-hexyloxy-vinylphosphonic acids have been synthesized by the action of alcohols in presence of pyridine on the corresponding 2-alkoxyvinylphosphonic dichlorides.

2. The dimethyl, diethyl, dipropyl, diisopropyl, dibutyl, diisobutyl, diallyl, dihexyl, bis(2-methoxyethyl), and bis(2-ethoxyethyl) esters of 2-ethoxy-, 2-propoxy-, 2-butoxy-, and 2-hexyloxy-vinylphosphonic acids have been prepared.

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* See Consultants Bureau Translation, p. 521.
** See Consultants Bureau Translation, p. 83.
*** See Consultants Bureau Translation, p. 423.
**** See Consultants Bureau Translation, p. 531

THE PRODUCTS OF THE ACTION OF SODIUM DIETHYL PHOSPHOROTHIONATE ON ALKYL PHOSPHORODICHLORIDITES

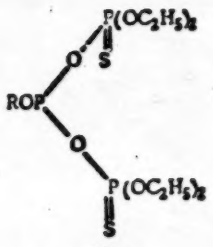
B. A. Arbuzov and P. I. Alimov

Derivatives of pyrophosphoric and triphosphoric acids and of their sulfur analogs are at present attracting much attention owing to the fact that pyrophosphoric and triphosphoric groupings have been found in some physiologically active compounds, such as vitamins, nucleotides, and coenzymes, and also because many derivatives of pyrophosphoric acid and its sulfur analogs have been found to be powerful insecticides.

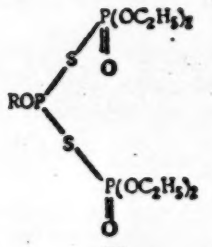
In this paper we describe the preparation and some of the properties of esters of an acid that can be regarded as an anhydride formed from two molecules of phosphorothionic acid and one molecule of phosphorous acid. Esters of general formula ROP $[OPS(OC_2H_5)_2]_2$ have been prepared by us for the first time by the action of sodium diethyl phosphorothionate on alkyl phosphorodichloridites, which proceeds according to the equation

$$ROPCl_2 + 2NaOPS(OC_2H_5)_2 = ROP[OPS(OC_2H_5)_2]_2 + 2NaCl.$$

Sodium diethyl phosphorothionate was prepared by the addition of sulfur to sodium diethyl phosphite. The structure of the reaction products can be represented by formulas in which phosphorus atoms are united through oxygen or sulfur



(I)



(II)

On the basis of the method of preparation from sodium diethyl phosphorothionate, formula (I) appears to be more probable but as it is possible that sodium may move from oxygen to sulfur, the question of which of the formulas (I) and (II) represents the structure of these compounds must remain open.

In the preparation of the alkyl phosphite – diethyl phosphorothionate anhydrides the alkyl phosphorodichloridites used as starting materials were methyl, ethyl, propyl, isopropyl, and isobutyl phosphorodichloridites. When treated with sodium diethyl phosphorothionate, these acid chlorides yielded the compounds listed with their constants in the table.

TABLE 1

No.	R	B.p. in °C (p in mm Hg)	n_D^{20}	d_4^{20}	Yield (%)
1	CH_3	164-165 (2)	1.4837	1.2287	22.8
2	C_2H_5	160-161 (1)	1.4815	1.2069	25.4
3	i-C_3H_7	170-171 (3.5)	1.4800	1.1863	8.8
4	n-C_3H_7	168-169 (2.5)	1.4780	1.1901	32.4
5	i-C_4H_9	166-167 (1.5)	1.4802	1.1747	40.2

All of the substances given in the table are colorless mobile liquids having odors characteristic of sulfur compounds. They are soluble in water and in organic solvents. The yields of the pure substances were 20-40%. One of the causes of the low yields of the products is their instability at the high temperatures employed in the distillation (bath temperature 200-215°). These anhydrides of alkyl hydrogen phosphite with diethyl hydrogen phosphorothionate react with cuprous halides stoichiometrically with evolution of heat (A. E. Arbuzov's reaction for

tervalent phosphorus), but we have not succeeded in isolating individual products, noncrystallizing syrups being obtained.

In spite of the fact that one of the phosphorus atoms of the compounds described is tervalent, they do not unite with sulfur under the conditions that result in the ready addition of sulfur to other organophosphorus compounds, e.g. trialkyl phosphites.

EXPERIMENTAL

1. The Ethyl Phosphite – Diethyl Phosphorothionate Anhydride $C_2H_5OP[OPS(OC_2H_5)_2]_2$.

Sodium diethyl phosphorothionate was prepared from 30.2 g of diethyl hydrogen phosphite, 5 g of sodium, and 7 g of sulfur in 100 ml of gasoline (b.p. 70-125°), and the mixture was stirred at room temperature while ethyl phosphorodichloridite was added slowly. The flask and contents were heated in a water bath and then cooled. Sodium chloride was centrifuged off, and gasoline was distilled off under reduced pressure. The residue (30 g, i.e. 66.3%) was fractionated, and the following fractions were obtained at a residual pressure of 1 mm:

Fraction I,	B.p. 85-150°;	4 g
Fraction II,	B.p. 150-160°;	6 g
Fraction III,	B.p. 160.5-161°;	12 g

Redistillation of Fractions II and III yielded 11.5 g (25.4%) of a substance of b.p. 160-161° (1 mm); n_D^{20} 1.4915; d_4^{20} 1.2069.

	Found %:	P 22.31; 22.32; S 15.32; 15.37
$C_{16}H_{35}P_3S_2O_7$.	Calculated %:	P 22.46; S 15.46

It was a colorless mobile liquid having a sulfurous odor. It was soluble in water and in organic solvents.

2. The Methyl Phosphite – Diethyl Phosphorothionate Anhydride $CH_3OP[OPS(OC_2H_5)_2]_2$.

Sodium diethyl phosphorothionate was prepared in gasoline from 27.2 g of diethyl hydrogen phosphite, 4.5 g of sodium, and 6.3 g of sulfur, and 13.1 g of methyl phosphorodichloridite was added. The yield of crude product was 29.8 g (75.6%) (a pale-yellow mobile liquid). The first distillation from an Arbuzov flask at 2 mm gave the following fractions:

Fraction I,	B.p. 75-154°;	3.2 g
Fraction II,	B.p. 154-162°;	3.3 g
Fraction III,	B.p. 162-165°;	10.5 g
Residue		12 g

Refractionation of Fractions II and III yielded 9 g (28.8%) of a substance of b.p. 164-165°; (2 mm); n_D^{20} 1.4837; d_4^{20} 1.2287

	Found %:	P 23.03; 23.03; S 15.75; 15.69
$C_9H_{23}P_3S_2O_7$.	Calculated %:	P 23.25 S 16.00

3. The Isopropyl Phosphite – Diethyl Phosphorothionate Anhydride $i\text{-}C_3H_7OP[OPS(OC_2H_5)_2]_2$

The reactants were 17.5 g of isopropyl phosphorodichloridite and sodium diethyl phosphorothionate prepared from 30 g of diethyl hydrogen phosphite, 5 g of sodium, and 6.9 g of sulfur. The reaction was carried out in gasoline (b.p. 75-125°). The yield of crude product was 35 g (88.3%) (a mobile yellowish-green liquid). The first distillation was carried out at 4 mm in a Claisen flask having a low delivery tube. The fractions obtained were:

Fraction I	B.p. to 145°;	4 g
Fraction II	B.p. 145-171°;	9 g
Fraction III	B.p. 171-176°;	3.5 g
Residue		17 g

Refractionation of Fractions II and III was carried out from an Arbuzov flask. The product was 3.5 g (8.8%) of a substance of b.p. 170-171° (3.5 mm); n_D^{20} 1.4800; d_4^{20} 1.1863.

	Found %:	P 21.61; 21.8; S 14.9; 15.08
$C_{11}H_{27}P_3S_2O_7$.	Calculated %:	P 21.72; S 14.95

4. The Propyl Phosphite – Diethyl Phosphorothionate Anhydride $n\text{-}C_3H_7OP[OPS(OC_2H_5)_2]_2$

Propyl phosphorodichloridite (19 g) was added to sodium diethyl phosphorothionate prepared from 32.6 g of

diethyl hydrogen phosphite, 5.4 g of sodium, and 7.5 g of sulfur in 100 ml of gasoline (b.p. 70-125°). The yield of crude product was 41.2 g (81.5%). Two distillations yielded a fraction of b.p. 168-169° (2.5 mm); n_D^{20} 1.4780; d_4^{20} 1.1901. The yield was 16.4 g (32.4%).

Found %: P 21.43; 21.61

$C_{11}H_{27}P_3S_2O_7$. Calculated %: P 21.72

This substance was a mobile liquid, readily soluble in water and in organic solvents.

5. The Isobutyl Phosphite – Diethyl Phosphorothionate Anhydride $i\text{-}C_4H_9OP[OPS(OC_2H_5)_2]_2$.

This was prepared by the same procedure by the action of isobutyl phosphorodichloridite (17.2 g) on sodium diethyl phosphorothionate prepared from 27.2 g of diethyl hydrogen phosphite, 4.5 g of sodium, and 6.3 g of sulfur. Two distillations of the crude product from an Arbuzov flask yielded a fraction of b.p. 166-167° (1.5 mm); n_D^{20} 1.4802; d_4^{20} 1.1747. The yield was 17.5 g (40.2%).

Found %: P 21.09; 20.75; S 14.66; 14.62

$C_{12}H_{29}P_3S_2O_7$. Calculated %: P 21.04; S 14.48

6. Action of Cuprous Bromide on the Ethyl Phosphite – Bis[Diethyl Phosphorothionate] Anhydride.

The ester (1.2 g) was placed in a test tube, and an equimolecular amount (0.41 g) of cuprous bromide was added. Part of the salt dissolved at room temperature, and the temperature of the mixture rose from 24° to 35°. The test tube was heated in an oil bath at 140-150°. The whole of the salt rapidly dissolved, and a clear solution was formed. The resulting viscous liquid did not crystallize even after standing for a long time.

SUMMARY

By the action of alkyl phosphorodichloridites $ROPCl_2$ (R= methyl, ethyl, isopropyl, propyl, and isobutyl) on sodium diethyl phosphorothionate $(C_2H_5O)_2PSONa$, anhydrides of alkyl dihydrogen phosphite with two molecules of diethyl hydrogen phosphorothionate of general formula $ROP[OPS(OC_2H_5)_2]_2$ have been prepared for the first time, and some of their properties have been studied.

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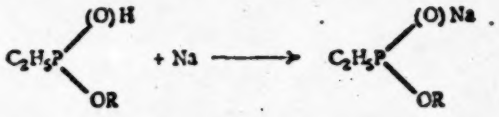
ESTERS OF ETHYLPHOSPHONOUS ACID, AND SOME OF THEIR REACTIONS

COMMUNICATION 5. SYNTHESIS OF ESTERS OF DIALKYLPHOSPHINIC ACIDS

B. A. Arbuzov and N. I. Rizpolozhensky

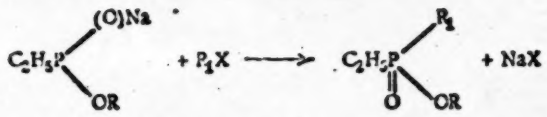
Continuing our study of the monoesters of the ethylphosphonous acid that we have synthesized [1], we have prepared some esters of dialkylphosphinic acids. We have already [2] prepared some dialkylphosphinic esters, including some containing unlike radicals on the phosphorus, by application of the Arbuzov rearrangement [3] in a study of the chemical properties of the diesters of ethylphosphonous acid, but it should be noted that the yields of the mixed-radical esters were rather low (25-30%).

Razumov and Mukhacheva [4] prepared dialkylphosphinic esters by the action of alcohols on dialkylphosphinic chlorides. Michaelis and Becker [5] showed that sodium dialkyl phosphites react with certain halogen compounds with formation of esters of alkylphosphonic acids, and we considered that it would be of interest to examine the possibility of applying this reaction for the synthesis of dialkylphosphinic esters, particularly those having unlike radicals on the phosphorus. It was found that the acid esters of ethylphosphonous acid, like those of phosphorous acid, react with sodium with formation of the sodium derivatives according to the equation



These sodium derivatives are soluble in ether, gasoline, and benzene.

Alkyl halides react with sodium alkyl ethylphosphonites with formation of dialkylphosphinic esters according to the equation:



Using this reaction we have prepared some dialkylphosphinic esters having unlike radicals on the phosphorus, and the yields have been satisfactory (50-60% on the average). The principal physicochemical constants of these esters are given in the table.

EXPERIMENTAL

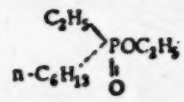
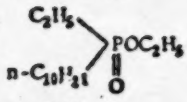
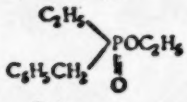
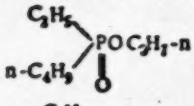
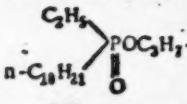
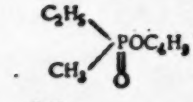
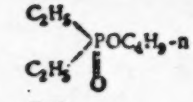
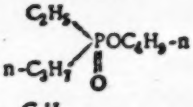
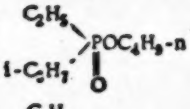
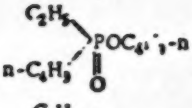
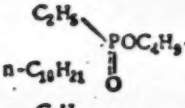
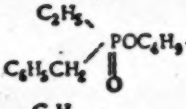
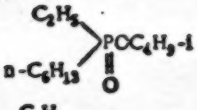
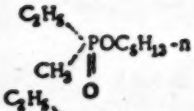
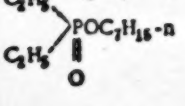
Synthesis of Dialkylphosphinic Esters

1. Ethyl Ethylhexylphosphinate. Ether (50-60 ml) and sodium (0.8 g, an excess) were placed in a three-necked flask fitted with a mercury-sealed mechanical stirrer, a reflux condenser, and a dropping funnel. Ethyl hydrogen ethylphosphonite (3.7 g) was added from the funnel, and the flask was heated in a water bath for 1.5-2 hours. The excess of sodium was then removed, and the ethereal solution of sodium ethyl ethylphosphonite was then boiled while addition was made of 6.4 g of hexyl iodine. The flask was heated for a further 1-1.5 hours in a water bath.

The precipitate of sodium iodide was removed by centrifugation. The residue remaining after removal of ether was vacuum-fractionated from an Arbuzov flask, and the ethyl ethylhexylphosphinate obtained had the following constants: b.p. 93° (0.5 mm); d_4^{20} 0.9302; n_D^{20} 1.4413.

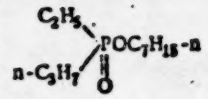
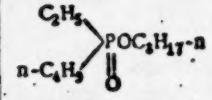
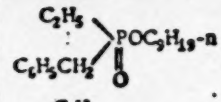
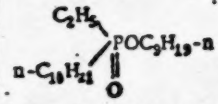
	Found:	MR 58.38
$C_{10}H_{23}PO_2$.	Calculated:	MR 58.33
	Found %:	P 14.85; 14.92
$C_{10}H_{23}PO_2$.	Calculated %:	P 15.03

TABLE*

No.	Formula	B.p. in °C (p in mm Hg)	d_4^{20}	n_D^{20}	MR found	MR calculated	Yield (%)
1		93 (0.5)	0.9302	1.4413	58.38	58.33	48
2		130-131 (1)	0.9160	1.4480	76.68	76.88	50
3		115-115.5 (1)	1.0793	1.5122	59.02	59.14	61
4		119-120 (10)	0.9483	1.4395	53.31	53.50	54
5		140-141 (1)	0.9129	1.4478	81.03	81.20	45
6		73-74 (1.5)	0.9689	1.4350	44.45	44.26	54
7		80-81 (0.5)	0.9588	1.4371	48.71	48.88	63
8		83-84 (0.5)	0.9461	1.4381	53.36	52.50	66
9		70-72 (0.5)	0.9452	1.4365	53.23	53.50	26
10		89-90 (0.5)	0.9372	1.4400	57.98	58.01	71
11		148-150 (1.5)	0.9083	1.4489	85.75	85.82	54
12		124-125 (0.5)	1.0397	1.5050	69.14	69.37	71
13		106-107 (0.5)	0.9235	1.4413	67.05	67.35	51
14		132-133 (12)	0.9483	1.4391	53.22	53.51	51
15		106-107 (0.5)	0.9332	1.4433	62.63	62.74	53

* In accordance with Kosolapoff's results [6], the atomic refraction of phosphorus is taken as 4.79.

TABLE 1 (Continued

No.	Formula	B.p. in °C (p in mm Hg)	d_4^{20}	n_D^{20}	MR found	MR calculated	Yield (%)
16		111-113 (0.5)	0.9262	1.4438	67.18	67.36	60
17		133-134 (1)	0.9159	1.4467	76.49	76.59	40
18		164-166 (0.5)	0.9814	1.4943	92.20	92.30	52
19		181-182 (0.5)	0.8947	1.4521	108.74	108.91	61

The yield of the ester was 3.1 g (48%).

In all of the succeeding experiments on the synthesis of dialkylphosphinic esters, the same procedure was employed.

2. Ethyl Decylethylphosphinate. The reactants were 2.8 g of ethyl hydrogen ethylphosphonite, 4.9 g of decyl bromide, and 0.8 g (an excess) of sodium. The resulting ester had the following constants: b.p. 130-131° (1 mm); d_4^{20} 0.9100; n_D^{20} 1.4480

Found: MR 76.68
$C_{14}H_{31}PO_2$. Calculated: MR 76.88
Found %: P 12.05; 11.86
$C_{14}H_{31}PO_2$. Calculated %: P 11.81

The yield of the ester was 3.1 g (50%).

3. Ethyl Benzylethylphosphinate. The reactants were 3 g of ethyl hydrogen ethylphosphonite, 4.2 g of benzyl bromide, and 1.2 g (an excess) of sodium. The principal constants of the ester were: b.p. 115-115.5° (1 mm); d_4^{20} 1.0793; n_D^{20} 1.5122.

Found: MR 59.02
$C_{11}H_{17}PO_2$. Calculated: MR 59.14
Found % P 14.48; 14.52
$C_{11}H_{17}PO_2$. Calculated % P 14.61

The yield of the ester was 3.2 g (61%).

4. Propyl Butylethylphosphinate. The reactants were 4.2 g of propyl hydrogen ethylphosphonite, 5.7 g of butyl iodide, and 0.9 g (an excess) of sodium. The constants of propyl butylethylphosphinate were: b.p. 119-120° (10 mm); d_4^{20} 0.9483; n_D^{20} 1.4395.

Found: MR 53.31
$C_9H_{21}PO_2$. Calculated: MR 53.50
Found %: P 15.92; 15.98
$C_9H_{21}PO_2$. Calculated %: P 16.12

The yield of the ester was 3.22 g (54%).

5. Propyl Decylethylphosphinate. The reactants were 3.5 g of propyl hydrogen ethylphosphonite 5.7 g of decyl bromide and 1.2 g (an excess) of sodium. The ester obtained had the following constants: b.p. 140-141.5° (1 mm); d_4^{20} 0.9129; n_D^{20} 1.4478.

Found: MR 81.03
$C_{15}H_{33}PO_2$. Calculated: MR 81.20
Found %: P 11.31; 11.23
$C_{15}H_{33}PO_2$. Calculated %: P 11.47

The yield of the ester was 3.2 g (45%).

6. Butyl Ethylmethylphosphinate. The reactants were 6 g of butyl hydrogen ethylphosphonite, 5.7 g of methyl iodide, and 1.7 g (an excess) of sodium. The ester obtained had the following constants: b.p. 73-74° (1.5 mm); d_4^{20} 0.9689; n_D^{20} 1.4350.

Found MR 44.45
$C_7H_{17}PO_2$. Calculated MR 44.26
Found %: P 19.21; 19.26
$C_7H_{17}PO_2$. Calculated %: P 18.76

The yield of the ester was 3.6 g (54%).

7. Butyl Diethylphosphinate. The reactants were 7 g of butyl hydrogen ethylphosphonite, 5.1 g of ethyl bromide and 1.5 g (an excess) of sodium. The ester obtained had b.p. 80-81° (0.5 mm); d_4^{20} 0.9588; n_D^{20} 1.4371.

Found: MR 48.71
$C_8H_{19}PO_2$. Calculated: MR 48.88
Found %: P 17.48; 17.63
$C_8H_{19}PO_2$. Calculated %: P 17.39

The yield of ester was 5.4 g (63%).

8. Butyl Ethylpropylphosphinate. The reactants were 6 g of butyl hydrogen ethylphosphonite, 4.9 g of propyl bromide, and 1.4 g (an excess) of sodium. The constants of the butyl ethylpropylphosphinate were as follows: b.p. 83-84° (0.5 mm); d_4^{20} 0.9161; n_D^{20} 1.4381.

Found: MR 53.36
$C_9H_{21}PO_2$. Calculated: MR 53.50
Found %: P 16.27; 16.15
$C_9H_{21}PO_2$. Calculated %: P 16.12

The yield of ester was 5.1 g (60%).

9. Butyl Ethylisopropylphosphinate. Butyl ethylisopropylphosphinate was synthesized from 5 g of butyl hydrogen ethylphosphonite, 4.1 g of isopropyl bromide, and 1.6 g (an excess) of sodium. This synthesis, unlike those previously described, was carried out not in diethyl ether, but in gasoline of b.p. 80-120°, since the reaction did not go in ether. The butyl ethylisopropylphosphinate obtained in this way had the following constants: b.p. 70-72° (0.5 mm); d_4^{20} 0.9452; n_D^{20} 1.4365.

Found: MR 53.23
$C_9H_{21}PO_2$. Calculated: MR 53.50
Found %: P 15.85; 16.05
$C_9H_{21}PO_2$. Calculated %: P 16.12

The yield was 1.7 g (26%).

10. Butyl Butylethylphosphinate. The reactants were 8 g of butyl hydrogen ethylphosphonite, 7.8 g of butyl bromide, and 1.6 g (an excess) of sodium. The principal constants of the ester were: b.p. 89-90° (0.5 mm); d_4^{20} 0.9372; n_D^{20} 1.4400.

Found: MR 57.98
$C_{10}H_{23}PO_2$. Calculated: MR 58.01
Found %: P 15.12; 15.22
$C_{10}H_{23}PO_2$. Calculated %: P 15.02

The yield of the ester was 7.8 g (71%).

11. Butyl Decylethylphosphinate. The reactants were 3.4 g of butyl hydrogen ethylphosphonite, 5 g of decyl bromide, and 0.9 g (an excess) of sodium. The constants of the ester obtained were as follows: b.p. 148-150° (1.5 mm); d_4^{20} 0.9083; n_D^{20} 1.4489.

Found: MR 85.75
$C_{16}H_{35}PO_2$. Calculated: MR 85.82
Found %: P 10.88
$C_{16}H_{35}PO_2$. Calculated %: P 10.67

The yield was 3.4 g (51%).

12. Butyl Benzylethylphosphinate. The reactants were 3.5 g of butyl hydrogen ethyl phosphonite, 4 g of benzyl bromide, and 0.8 g (an excess) of sodium. The constants of the ester were: b.p. 124-125° (0.5 mm); d_4^{20} 1.0397; n_D^{20} 1.5050.

Found : MR 69.14
$C_{13}H_{21}PO_2$. Calculated : MR 69.37
Found %: P 12.78; 13.05
$C_{13}H_{21}PO_2$. Calculated %: P 12.89

The yield was 4.1 g (71%).

13. Isobutyl Ethylhexylphosphinate. The reactants were 3.5 g of isobutyl hydrogen ethylphosphonite, 0.5 g of hexyl iodide, and 0.7 g (an excess) of sodium. The principal constants of the ester were : b.p. 106-107° (0.5 mm); d_4^{20} 0.9235; n_D^{20} 1.4413.

Found : MR 67.05
$C_{12}H_{27}PO_2$. Calculated : MR 67.35
Found %: P 13.36; 13.39
$C_{12}H_{27}PO_2$. Calculated %: P 13.24

The yield was 2.5 g (51%).

14. Hexyl Ethylmethylphosphinate. The reactants were 5.6 g of hexyl hydrogen ethylphosphonite, 4.5 g of methyl iodide, and 1.1 g (an excess) of sodium. The principal constants of the ester were: b.p. 132-134° (12 mm); d_4^{20} 0.9483; n_D^{20} 1.4391.

Found: MR 53.22
$C_{10}H_{23}PO_2$. Calculated: MR 53.51
Found %: P 16.22; 16.37
$C_{10}H_{23}PO_2$. Calculated %: P 16.12

The yield was 3.3 g (51%).

15. Heptyl Diethylphosphinate. The reactants were 5.5 g of heptyl hydrogen ethylphosphonite, 4.2 g of ethyl iodide, and 1.0 g (an excess) of sodium. The principal constants of the ester were: b.p. 106-107° (0.5 mm); d_4^{20} 0.9332; n_D^{20} 1.4433.

Found : MR 62.63
$C_{11}H_{25}PO_2$. Calculated : MR 62.74
Found %: P 14.12; 14.27
$C_{11}H_{25}PO_2$. Calculated %: P 14.07

The yield was 3.4 g (53%).

16. Heptyl Ethylpropylphosphinate. The reactants were 5.7 g of heptyl hydrogen ethylphosphonite, 3.6 g of propyl bromide, and 1.2 g (an excess) of sodium. The constants of the ester were: b.p. 111-113° (0.5 mm); d_4^{20} 0.9062; n_D^{20} 1.4438.

Found : MR 67.18
$C_{12}H_{27}PO_2$. Calculated : MR 67.36
Found %: P 13.19; 13.37
$C_{12}H_{27}PO_2$. Calculated %: P 13.22

Yield was 4.2 g (60%).

17. Octyl Butylethylphosphinate. The reactants were 6 g of octyl hydrogen ethylphosphonite, 5.4 g of butyl iodide, and 0.9 g (an excess) of sodium. The principal constants of the ester were: b.p. 133-134° (1 mm); d_4^{20} 0.9159; n_D^{20} 1.4467.

Found : MR 76.49
$C_{14}H_{31}PO_2$. Calculated : MR 76.59
Found %: P 11.63; 11.74
$C_{14}H_{31}PO_2$. Calculated %: P 11.81

The yield was 3.3 g (40%).

18. Nonyl Butylethylphosphinate. The reactants were 3.4 g of nonyl hydrogen ethylphosphonite, 2.6 g

of benzyl bromide, and 0.8 g (an excess) of sodium. The constants of the ester obtained were: b.p. 164-166° (0.5 mm); d_4^{20} 0.9814; n_D^{20} 1.4918.

	Found :	MR 92.20
$C_{18}H_{31}PO_2$.	Calculated :	MR 92.30
	Found % :	P 9.63; 9.68
$C_{18}H_{31}PO_2$.	Calculated % :	P 9.99

The yield was 2.5 g (52%).

19. Nonyl Decylethylphosphinate. The reactants were 4.5 g of nonyl hydrogen ethylphosphonite, 4.6 g of decyl bromide, and 0.9 g (an excess) of sodium. The principal constants of the ester were : b.p. 181-182° (0.5 mm); d_4^{20} 0.8917; n_D^{20} 1.4521.

	Found :	MR 108.74
$C_{21}H_{45}PO_2$.	Calculated :	MR 108.91
	Found % :	P 8.51; 8.64
$C_{21}H_{45}PO_2$.	Calculated % :	P 8.6

The yield was 4.5 g (61%).

SUMMARY

1. Is has been shown that acid esters of ethylphosphonous acid, like those of phosphorous acid, react with sodium to give sodium derivatives.

2. When sodium alkyl ethylphosphonites react with alkyl halides, alkylethylphosphinic esters are obtained.

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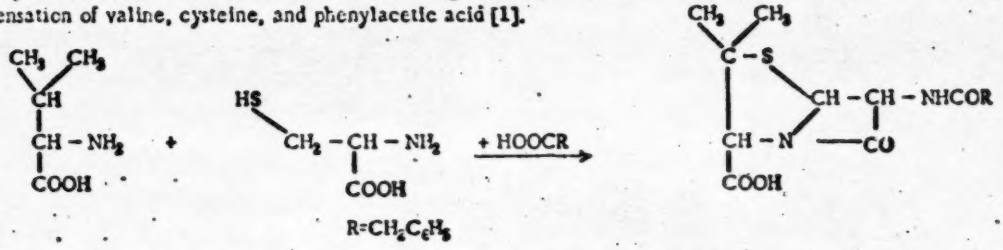
* See Consultants Bureau Translation, p. 843.
** " " " " 765

REACTIONS OF MERCAPTO AMINO ACIDS

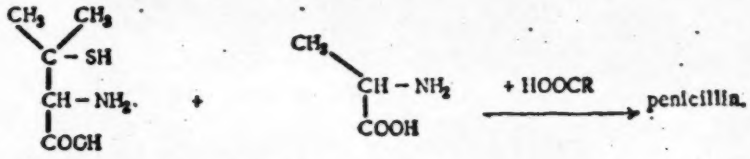
COMMUNICATION 4. N-ACYL-2,3-DIHALOALANINES

O. V. Kiidisheva, L. P. Rastelkene, and I. L. Knunyants

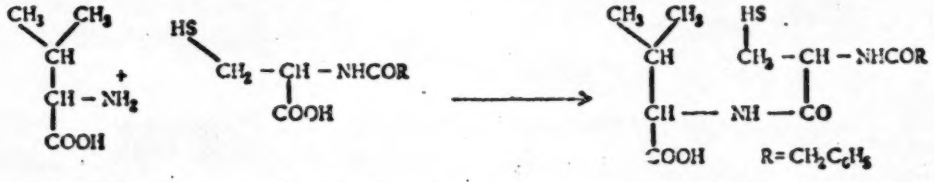
The search for antibiotics of the penicillin type has taken a new direction. Penicillin is a peculiar peptide, built up from several amino acids, and it is not altogether improbable that it is formed as a result of the enzymic condensation of valine, cysteine, and phenylacetic acid [1].



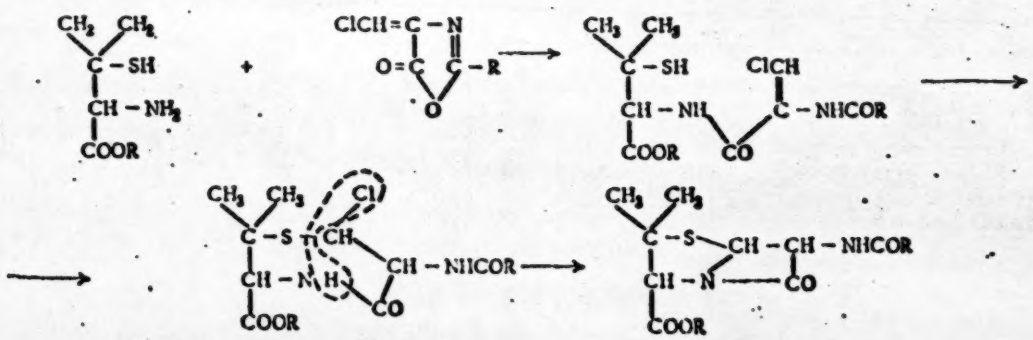
or, although this is less probable, of 3,3-dimethylcysteine, alanine, and phenylacetic acid



The coupling together of amino acids may be a promising line of approach to the synthesis of substances of the penicillin type. Recently, for example, a compound having an antibiotic activity of 12 units per mg has been obtained by the condensation of N-(phenylacetyl)-L-cysteine with D-valine [2].



In spite of the negative results of numerous investigations on the synthesis of penicillin, the problem of synthesizing this antibiotic cannot be regarded as insoluble. It is quite obvious that the final stage of its synthesis must be a process in which the conditions are such as to ensure the survival of the penicillin formed. Such a process might be provided by the reaction of 3,3-dimethylcysteine and its derivatives with 2-benzyl (or phenyl)-4-(halomethylene)-2-oxazolin-5-ones.



However, it has not yet been found possible to carry out this reaction. At present only one such oxazolinone is known, namely 4-(chloromethylene)-2-phenyl-2-oxazolin-5-one, which has been prepared by the action of thionyl chloride on the difficultly accessible 4-(hydroxymethylene)-2-phenyl-2-oxazolin-5-one [3]. The simplest method of preparing oxazolinones of this type would appear to be the dehydration of 2-(acylamino)-haloacrylic acids.

With a view to the preparation of various 2-(acylamino)-3-haloacrylic acids, methods of preparing 2-(acylamino) acrylic acids have been investigated and their properties have been studied. 2-(Acylamino)acrylic acids containing the following acylamino groups are now known: formamido [4, 5], acetamido [6], chloroacetamido [6,7], propionamido [8], benzamido [9-11], 2-phenacetamido [11-14], and benzyloxycarbonylamino [5].

A general method for the preparation of 2-(acylamino)acrylic acids consists in heating solutions of 2,2-bis(acylamino)propionic acids in glacial acetic acid:

$$CH_3-\underset{\underset{COOH}{|}}{C}(NHCOR)_2 \xrightarrow{CH_3COOH} CH_2=\underset{\underset{COOH}{|}}{C}-NHCOR + H_2NCOR$$

It should be noted that, even when the reaction is carried out with care, the resulting acylamino acrylic acid is sometimes hydrolyzed to a keto acid:

$$CH_2=\underset{\underset{COOH}{|}}{C}-NHCOR \xrightarrow{H_2O} CH_2=C\begin{matrix}OH\\ \diagdown\\ \diagup\\ COOH\end{matrix} \rightleftharpoons CH_3COCOOH,$$

Positive results in such experiments are therefore not always reproduced. A modification of this method of preparing 2-(acylamino)acrylic acids consists in heating an amide with excess of a keto acid:

$$CH_3COCOOH \xrightarrow{NH_2COR} CH_2=\underset{\underset{COOH}{|}}{C}-NHCOR + H_2O.$$

In 1946 L. Kraft showed that in presence of benzene (the water formed in the reaction distils over with the benzene as an azeotropic mixture) the yield of (acylamino)acrylic acid can be considerably increased, but he did not succeed in preparing 2-benzamidoacrylic acid by this method.

Investigation has shown that by variation in the amount of solvent and the duration of heating any 2-(acylamino)acrylic acid can be prepared by this method. The by-product of this reaction, the 2,2-bis(acylamino)propionic acid, can itself be converted into the 2-acylamino)acrylic acid by being heated with excess of the keto acid in benzene:

$$CH_3-\underset{\underset{COOH}{|}}{C}(NHCOR)_2 \xrightarrow{CH_3COCOOH} 2CH_2=\underset{\underset{COOH}{|}}{C}-NHCOR$$

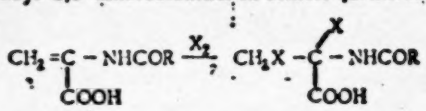
The yields of 2-(acylamino acrylic acids prepared by heating the corresponding amides with two molecular proportions of pyruvic acid in benzene are given in Table 1.

TABLE 1

2-(Acylamino)acrylic acid		Prepared from			Duration of heating (hours)	M.p. (°C)	Yield (%)
		$CH_3COCOOH$ (moles)	$RCONH_2$ (moles)	benzene (ml)			
$CH_2=\underset{\underset{COOH}{|}}{C}-NHCOCH_3$	(I)	0.5	0.25	500	4	198-199	53
$CH_2=\underset{\underset{COOH}{|}}{C}-NHCOC_6H_5$	(II)	0.46	0.2	600	20	158-160	30-35
$CH_2=\underset{\underset{COOH}{|}}{C}-NHCOCH_2C_6H_5$	(III)	0.4	0.2	300	6	189-190	40-50
$CH_2=\underset{\underset{COOH}{|}}{C}-NHCOOCH_2C_6H_5$	(IV)	0.2	0.1	300	2-3	100-101	43

The double bond of 2-(acylamino)acrylic acids has not lost its power of taking part in addition reactions. For example, in presence of peroxide catalysts 2-(acylamino)acrylic acids readily polymerize with formation of new polymers having unusual properties [5, 15, 16]. Esters of (acylamino)acrylic acids will polymerize even in absence of catalysts [10, 15-18]. 2-(Acylamino)acrylic acids are hydrogenated in presence of catalysts with formation of alanine derivatives [6, 19]. Amines add to them with formation of 2-(acyl amino)-3-(alkylamino)propionic acids [20, 21]. They unite with amides with formation of bis(acylamino)propionic acids [22, 23], and they react with diazomethane, which converts them into derivatives of pyrazolidinecarboxylic acid [6]*. The addition to 2-(acylamino)acrylic acids of hydrogen sulfide [10], thiols [24], and thioacetic acid [25, 26] has provided a practical means of preparing α-amino β-mercapto acids and their derivatives, such as lanthionine [27] and dimethyllanthionine [13]. 2-(Acylamino)acrylic acids unite readily also with hydrogen halides with formation of N-acyl-3-haloalanines, but their behavior towards the halogens has not been studied.

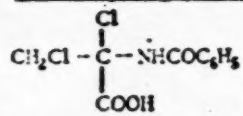
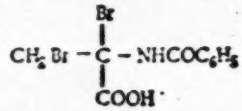
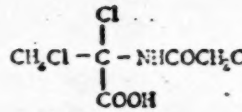
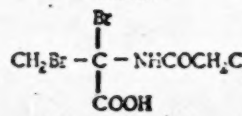
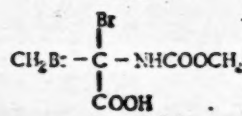
An investigation of the halogenation of 2-(acylamino)acrylic acids has shown that both chlorine and bromine readily add with formation of N-acyl-2,3-dihaloalanines in almost quantitative yields:



(V) X=Cl, R=C_6H_5; (VI) X=Br, R=C_6H_5; (VII) X=Cl R=$CH_2C_6H_5$; (VIII) X=Br, R=$CH_2C_6H_5$; (IX) X=Br, R=$OCH_2C_6H_5$.

Halogenation is effected readily at room temperature by means of 10% solutions of chlorine and bromine in dry chloroform or carbon tetrachloride. N-Acyl-2,3-dihaloalanines are insoluble in chloroform, but readily soluble in ether. They crystallize from ether as colorless needles having characteristic melting points (Table 2).

TABLE 2

N-Acyl-2,3-dihaloalanine		M.p. (°C)	Yield (%)
	(V)	128-130 (decomp.)	98
	(VI)	139-140 (decomp.)	93
	(VII)	105-107 (decomp.)	93
	(VIII)	128-130 (decomp.)	72
	(IX)	109-112 (decomp.)	96

It was found that the N-acyl-2,3-dihaloalanines obtained were extremely reactive. When the N-acyl-2,3-dibromoalanines were given prolonged treatments with water or aqueous alkaline solutions, complete hydrolysis occurred with formation of ammonium bromide. Heating for a short time with dilute alkali was sufficient to remove bromine completely, and the bromine could then be titrated quantitatively by the Volhard method. The dichloro acids were found to be more stable than the dibromo compounds; under the same conditions only one chlorine atom was removed, the second being hydrolyzed only after prolonged heating.

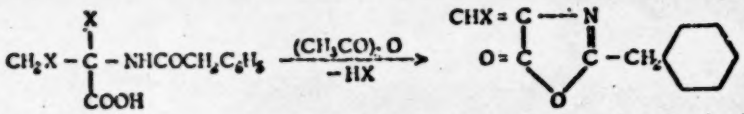
Acid hydrolysis of N-benzoyl-2,3-dibromoalanine (VI) and 2,3-dibromo-N-(phenylacetyl)alanine (VIII) resulted in the formation of different keto acids depending on the conditions. After a short hydrolysis addition of 2,4-dinitrophenylhydrazine precipitated the 2,4-dinitrophenylhydrazones of the previously unknown (benzoyloxy)- and (phenylacetoxy)-pyruvic acids (X and XI), m.p. 169-171° (decomp.) and 168-173° (decomp), respectively.

Longer hydrolysis of either compound resulted in the formation of hydroxypyruvic acid, which was isolated in the form of its known 2,4-dinitrophenylhydrazone, m.p. 160-161° [28]. The mechanism by which these keto acids were formed was elucidated by a study of the properties of N-acyl-3-halo-2-hydroxyalanines**. Further investigation

* 2-(2-Phenylacetamido)acrylic acid reacts normally with the theoretical amount of diazomethane at a low temperature, the corresponding ester being formed [14].

** See Communication 5 in this issue.

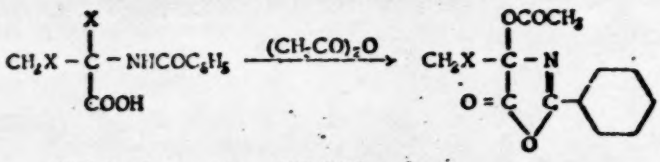
of the properties of N-acyl-2,3-dihaloalanines showed that, when 2,3-dichloro- and 2,3-dibromo-N-(phenylacetyl) alanines were heated in carbon tetrachloride or chloroform solution with acetic anhydride, reaction readily occurred with evolution of HCl or HBr and formation of the previously unknown 2-benzyl-4-(chloromethylene)-2-oxazolin-5-one (XII) and the corresponding bromomethylene compound (XIII):



(XII) X = Cl, M.p. 114-115° (decomp.)
(XIII) X = Br, M.p. 112-114° (decomp.)

A convenient method has thys been found for the preparation of difficultly accessible unsaturated 2-benzyloxazolinones.

It was found, unexpectedly, that N-benzoyl-2,3-dihaloalanines, unlike the N-(phenylacetyl) compounds, were converted by reaction under the same conditions into stable saturated 4-acetoxy-4-(halomethyl)-2-phenyl-2-oxazolin-5-ones (XIV) and (XV):



(XIV) X = Br, M.p. 137-138°.

(XV) X = Cl, M.p. 110°.

A separate communication will be devoted to a study of the properties of the oxazolinones obtained.

EXPERIMENTAL

2-Acetamidoacrylic Acid (I). A mixture of 35 g (0.4 mole) of freshly distilled anhydrous pyruvic acid, 12 g (0.2 mole) of acetamide, and 300 ml of absolute benzene was boiled with simultaneous distillation of benzene in a Dean and Stark apparatus until the separation of water ceased (four hours). The crystalline precipitate that formed was filtered off and washed with ether. The 2-acetamidoacrylic acid was extracted with acetone. The yield of the acid (I) (m.p. 198-199°) was 14 g (53%).

2-Benzamidoacrylic Acid (II). A mixture of 40 g (0.46 mole) of freshly distilled anhydrous pyruvic acid, 24.2 g (0.2 mole) of benzamide, and 600 ml of absolute benzene was boiled with simultaneous distillation of benzene in a Dean and Stark apparatus (about 14 hours). The benzene solution was filtered and extracted with a 10% solution of sodium carbonate. The alkaline solution was separated and acidified to Congo Red with 30% sulfuric acid. The precipitate that formed was filtered off, washed with water, dried, and then dissolved in three times its amount of ethyl acetate (by heating for five minutes). The undissolved bis(benzamido)propionic acid was filtered off, and the filtrate was extracted with a 10% solution of sodium carbonate. The alkaline solution was acidified to Congo Red at not above 10° with 30% sulfuric acid, and the precipitate that formed was filtered off, washed repeatedly with water, and dried. The product was 11.5 g (30%) of 2-benzamidoacrylic acid melting at 150-152°. Recrystallization from aqueous alcohol raised the melting point to 158-160°.

$C_{10}H_9O_3N$. Found %: C 62.72; H 4.82; N 7.95
Calculated %: C 62.8; H 4.72; N 7.93

2-(2-Phenylacetamido)acrylic Acid (III). a) A mixture of 35 g (0.4 mole) of freshly distilled anhydrous pyruvic acid, 27 g (0.2 mole) of 2-phenylacetamide, and 300 ml of absolute benzene was boiled under the conditions described above for six hours. The crystalline precipitate that formed was filtered off, washed with ether and with glacial acetic acid (to remove the bis(2-phenylacetamido)propionic acid by-product), and then washed again with ether.

The yield of 2-(2-phenylacetamido)acrylic acid, m.p. 178-180°, was 50-60%. After repeated recrystallization of the acid from aqueous alcohol its melting point was 189-190°.

$C_{11}H_{11}O_3N$. Found %: C 64.91; H 5.47
Calculated %: C 64.4; H 5.36

2-(2-Phenylacetamido)acrylic acid is readily soluble in alcohol and acetone, and can be crystallized from isopropyl alcohol or aqueous acetone.

b) A mixture of 17.6 g (0.2 mole) of pyruvic acid, 34.0 g (0.1 mole) of bis(2-phenylacetamido)propionic acid, and 135 ml of absolute benzene was boiled in a Dean and Stark apparatus for 18 hours. The crystalline precipitate was filtered off and purified as in the preceding experiment. The product was 24.5 g (59%) of 2-(2-phenylacetamido) acrylic acid, m.p. 174-176°.

2-(Benzyloxycarbonylamino)acrylic Acid (IV). Benzyl carbamate $NH_2COOCH_2C_6H_5$ was prepared either by the action of ammonia on benzyl chloroformate [29] or by the condensation of urea with benzyl alcohol in presence of stannic chloride [30]. A mixture of 17.6 g (0.2 mole) of freshly distilled anhydrous pyruvic acid, 15.1 g (0.1 mole) of benzyl carbamate, and 300 ml of absolute benzene was boiled under the conditions described above for three hours. The benzene solution was extracted with a saturated solution of sodium bicarbonate, and the uncharged benzyl carbamate (3.4 g) was filtered off. The alkaline solution was extracted with 50 ml of ether and acidified to Congo Red with concentrated hydrochloric acid. The oil that separated quickly solidified, and was then filtered off, washed with a small amount of water, and dried in a vacuum desiccator over P_2O_5. The product was 9.5 g (43%) of 2-(benzyloxycarbonylamino)acrylic acid, m.p. 100-101° (from benzene) *.

	Found %:	C 60.2; H 4.95
$C_{11}H_{11}O_4N$.	Calculated %:	C 59.72; H 5.0

When the same reaction was carried out with equimolecular amounts of reactants, bis(benzyloxycarbonylamino)-propionic acid of m.p. 134-136° (from 70% alcohol) was formed quantitatively.

2-(Benzyloxycarbonylamino)acrylic acid is readily soluble in alcohol, ether, and chloroform; it may be crystallized from aqueous alcohol, benzene, and toluene. When treated with acids and alkalis, it decomposes rapidly with formation of benzyl carbamate. It polymerizes when kept for a long time.

N-Benzoyl-2,3-dichloroalanine (V). Under cooling with ice water, 9.6 g (0.05 mole) of 2-benzamidoacrylic acid was treated with excess of chlorine dissolved in carbon tetrachloride (7.1 g of chlorine in 71 ml of carbon tetrachloride). Reaction proceeded with appreciable evolution of heat, and after 1-2 minutes a crystalline precipitate began to form in the clear solution. After an hour the precipitate was filtered off, washed, and dried. The product was 13.1 g (98%) of N-benzoyl-2,3-dichloroalanine, and after recrystallization from absolute ether is melted at 128-130° with decomposition. N-Benzoyl-2,3-dichloroalanine is a stable colorless crystalline compound. It is readily soluble in absolute ether, but insoluble in chloroform and carbon tetrachloride. A mixture of 0.1035 g of N-benzoyl-2,3-dichloroalanine, 15 ml of ethanol, and 2 g of sodium was boiled for one hour, after which the solution was cooled and diluted with water. The solution was acidified with concentrated nitric acid, and halogen was determined by Volhard titration.

	Found %:	Cl 27.0
$C_{10}H_9O_3NCl_2$.	Calculated %:	Cl 27.1

A weighed amount of N-benzoyl-2,3-dichloroalanine was dissolved in 0.5 N NaOH, and after one hour the solution was acidified with concentrated nitric acid and the halogen determined by Volhard titration.

	Found %:	Cl 15.6
$C_{10}H_9O_3NCl$.	Calculated %:	Cl 15.8

N-Benzoyl-2,3-dibromoalanine (VI). 2-Benzamidoacrylic acid (11.4 g, i.e. 0.06 mole) was dissolved in 96 ml of chloroform containing 9.6 g (0.06 mole) of bromine. Reaction occurred with appreciable evolution of heat, and after 1-2 minutes a crystalline precipitate began to form in the clear solution**. After 30 minutes the precipitate was filtered off, washed with dry chloroform, and dried in a vacuum desiccator over phosphoric oxide. The product was 19.5 g (93%) of N-benzoyl-2,3-dibromoalanine, which, after recrystallization from absolute ether, melted with decomposition at 139-140°. An accurately weighed amount of the dibromo acid was dissolved in 0.5 N NaOH at 50-60°. After 5-7 minutes the solution was cooled, acidified with concentrated nitric acid, and titrated by the Volhard method.

	Found %:	Br 43.7
$C_{10}H_9O_3NBr_2$.	Calculated %:	Br 45.6

N-Benzoyl-2,3-dibromoalanine is a stable colorless crystalline compound. When kept in a moist atmosphere, the acid decomposes with evolution of hydrogen bromide.

2,3-Dichloro-N-(phenylacetyl)alanine (VII). 2-(2-Phenylacetamido)acrylic acid (10.25 g, i.e. 0.05 mole) was treated with excess of chlorine by shaking it with a solution of 5.5 g of chlorine in 55 g of carbon tetrachloride. Chlorination occurred with appreciable evolution of heat. The reaction mixture was left at room temperature overnight, and on the next day the precipitate was filtered off, washed with chloroform, and dried. The yield of 2,3-di-

* The acid (IV) has been prepared independently from 2,2-bis(benzyloxycarbonylamino)propionic acid; it melted at 105° [5].

** 2-Benzamidoacrylic acid may sometimes contain some bis(benzamido)propionic acid as impurity. The latter is quite insoluble in ether, and is readily removed when the N-benzoyl-2,3-dibromoalanine is crystallized from ether.

chloro-N-(phenylacetyl)alanine was 12.75g (93%), and after recrystallization from absolute ether it melted with decomposition at 105-107°. A mixture of 0.2100 g of 2,3-dichlor-N-(phenylacetyl)alanine, 15 ml of absolute alcohol, and 2 g of sodium was boiled for one hour and then cooled and diluted with water. After acidification of the solution with concentrated nitric acid, halogen was determined by Volhard titration.

Found %: Cl 26.0
$C_{11}H_{11}O_3NCl_2$. Calculated %: Cl 25.7

2,3-Dibromo-N-(phenylacetyl)alanine (VIII). 2-(2-Phenylacetamido)acrylic acid (20.5 g, i.e. 0.1 mole) was treated with a solution of 16 g (0.1 mole) of bromine in 160 ml of chloroform. Bromination occurred with appreciable evolution of heat. The reaction mixture was left at room temperature overnight, and on the next day 20 ml of absolute ether was added and the mixture was refluxed with exclusion of moisture. The undissolved residue of bis(2-phenylacetamido)propionic acid, sometimes present as impurity, was filtered off, and the clear solution was set aside in a refrigerator. After 2-3 hours the crystalline precipitate that formed was filtered off, washed with dry chloroform, and dried in a vacuum desiccator over phosphoric oxide. The product was 20.5 g (73%) of 2,3-dibromo-N-(phenylacetyl) alanine, which formed colorless needles melting with decomposition at 128-130°.

An accurately weighed amount of the dibromo acid was dissolved in an excess of 0.5 N NaOH, and the solution was heated for five minutes at 50-60°. It was then cooled, acidified with concentrated nitric acid, and titrated for bromine by the Volhard method.

Found %: Br 42.9
$C_{11}H_{11}O_3NBr_2$. Calculated %: Br 43.8

In absence of moisture 2,3-dibromo-N-(phenylacetyl)alanine is a stable compound, readily soluble in ether and ethyl acetate, and almost insoluble in chloroform. It is readily decomposed by alcohol and by water, and when kept in a moist atmosphere it loses hydrogen bromide and is converted into 3-bromo-2-hydroxy-N-(phenylacetyl)alanine.

N-(Benzyloxycarbonyl)-2,3-dibromoalanine (IX). 2-(Benzyloxycarbonylamino)acrylic acid (9 g, i.e. 0.04 mole) was treated with a solution of 6.5 g (0.04 mole) of bromine in 65 ml of chloroform. Reaction occurred with evolution of heat, and after a few minutes a crystalline precipitate began to form in the clear solution. The reaction mixture was left in a refrigerator for 20 minutes, and the precipitate was then filtered off, washed with chloroform, and dried in a vacuum desiccator over phosphoric oxide. The yield of N-(benzyloxycarbonyl)-2,3-dibromoalanine was 14.8 g (96%); it melted with decomposition at 108-112°.

Found %: Br 41.4 (Volhard titration)
$C_{11}H_{11}O_4NBr_2$. Calculated %: Br 42

Bromine was determined as in the previous experiment. N-(Benzyloxycarbonyl)-2,3-dibromoalanine is insoluble in chloroform, benzene, and toluene, but very soluble in ether. It decomposes rapidly when kept in a moist atmosphere.

Acid Hydrolysis of N-Acyl-2,3-dibromoalanines

2,4-Dinitrophenylhydrazone of (Benzoyloxy)pyruvic Acid (X). N-Benzoyl-2,3-dibromoalanine (6.5 g, i.e. 0.018 mole) was dissolved at 55° in 100 ml of water. The solution was cooled, filtered, and treated with a 0.5% solution of 2,4-dinitrophenylhydrazine in 2 N HCl (800 ml). On the next day the crystalline precipitate was filtered off, washed with a small amount of water, and dried in a vacuum desiccator over phosphoric oxide. The yield of the 2,4-dinitrophenylhydrazone of (benzoyloxy)pyruvic acid, m.p. 168-173° (from alcohol), was 6.9 g (96.5%).

Found %: C 49.10; H 3.07
$C_{16}H_{12}O_8N_4$. Calculated %: C 49.4; H 3.09

2,4-Dinitrophenylhydrazone of (Phenylacetoxy)pyruvic Acid (XI). 2,3-Dibromo-N-(phenylacetyl)alanine (3.6 g, i.e. 0.01 mole) was warmed with 40 ml of water until dissolved (1-2 minutes), and the resulting solution was then rapidly cooled, filtered, and treated with a 0.5% solution of 2,4-dinitrophenylhydrazine in 2 N HCl (400 ml), when a yellow precipitate of the hydrazone was formed immediately. On the next day the precipitate was filtered off, washed with a small amount of water, and dried in a vacuum desiccator over phosphoric oxide. The yield of the 2,4-dinitrophenylhydrazone of (phenylacetoxy)pyruvic acid, m.p. 169-171° (from alcohol), was 3.85 g (95.8%).

Found %: C 50.5; H 3.3; N 15.1
$C_{17}H_{14}O_8N_4$. Calculated %: C 50.7; H 3.48; N 13.9

2,4-Dinitrophenylhydrazone of Hydroxypyruvic Acid. 2,3-Dibromo-N-(phenylacetyl)alanine (3.6 g, i.e. 0.01 mole) was warmed with 40 ml of water until dissolved (1-2 minutes at 70-80°). The solution was cooled and filtered, and was then left at room temperature for two days. The solution was evaporated down until crystallization began,

the crystalline precipitate of phenylacetic acid was filtered off, and the mother liquor was evaporated to dryness. The dry residue was dissolved in 150 ml of water, and the resulting solution was filtered and treated with a 0.5% solution of 2,4-dinitrophenylhydrazine in 2 N HCl (400 ml). The mixture was left overnight in a refrigerator, and on the next day the hydrazone was filtered off, washed with a small amount of water, and dried in a vacuum desiccator over phosphoric oxide. The product was 0.8 g (32%) of the 2,4-dinitrophenylhydrazone of hydroxypyruvic acid, m.p. 160-161° (from ethyl acetate). There was no depression in a mixture melting test with a sample of the 2,4-dinitrophenylhydrazone of hydroxypyruvic acid prepared by another method (from bromopyruvic acid [28]).

2-Benzyl-4-(chloromethylene)-2-oxazolin-5-one (XII). 2-(2-Phenylacetamido)acrylic acid (10 g, i.e. 0.05 mole) was treated with a solution of 3.55 g of chlorine in 50 ml of carbon tetrachloride). The reaction mixture was shaken for 30 minutes at room temperature and then set aside overnight. On the next day 50 ml of acetic anhydride was added, and carbon tetrachloride was removed at 40-55° at a residual pressure of 50 mm, which was then reduced to 4 mm. Acetic anhydride was then distilled off until crystallization began. The residue was diluted with a little absolute ethanol and then filtered off. It was washed, first with a little absolute alcohol, and then with ether. The product was 6.5 g (58%) of 2-benzyl-4-(chloromethylene)-2-oxazolin-5-one, which formed yellowish needles, melting with decomposition at 114-115° after recrystallization from absolute alcohol.

	Found %:	C 60.22; H 3.72; N 6.44
$C_{11}H_8O_2NCl$.	Calculated %:	C 59.2; H 3.63; N 6.33

2-Benzyl-4-(chloromethylene)-2-oxazolin-5-one is readily soluble in chloroform and ether, may be crystallized from alcohol, and is insoluble in water. It slowly decomposes (in 2-3 months) when kept in a moist atmosphere. With pyridine and pyridine bases it gives a green-blue coloration characteristic of (halomethylene)oxazolinones.

2-Benzyl-4-(bromomethylene)-2-oxazolin-5-one (XIII). 2-(2-Phenylacetamido)acrylic acid (10 g, i.e. 0.05 mole) was brominated in the way described above for the substance (VIII). On the next day 50 ml of acetic anhydride was added to the reaction mixture. The procedure adopted for the isolation of the oxazolinone (XIII) was exactly the same as that adopted for the isolation of (XII). The yield of 2-benzyl-4-(bromomethylene)-2-oxazolin-5-one was 7 g (52%); it melted at 110-112° (from absolute ether). It was found that the oxazolinone could be purified also by dissolution in chloroform and addition of absolute alcohol until a turbidity appeared. Completely pure crystals of m.p. 112-114° were precipitated.

	Found %:	C 49.80; H 3.07; N 5.5; Br 30.02
$C_{11}H_8O_2NBr$.	Calculated %:	C 49.62; H 3.00; N 5.2; Br 30.07

The oxazolinone (XIII) is very soluble in chloroform and is readily soluble also in alcohol, ether, and ethyl acetate. It gives a bluish-violet color with pyridine. It is hydrolyzed by alkali with formation of 3-bromo-2-(2-phenylacetamido)acrylic acid, m.p. 173°.

4-Acetoxy-4-(bromomethyl)-2-phenyl-2-oxazolin-5-one (XIV). 2-Benzamidoacrylic acid (9.5 g, i.e. 0.05 mole) was treated with a solution of 8 g of bromine in 80 ml of chloroform. After 30 minutes 50 ml of acetic anhydride was added, and the mixture was distilled under reduced pressure at 50-60°. After the distillation, the crystalline residue was filtered off, washed with a small amount of absolute ether, and dried in a vacuum desiccator over phosphoric oxide. The product was 6.8 g of the oxazolinone (XIV), m.p. 137-138° (from absolute alcohol). A further 4.2 g of the oxazolinone was obtained from the mother liquor, and the total yield was 70%. An 80% yield of the oxazolinone (XIV) was obtained from crystalline N-benzoyl-2,3-dibromoalanine.

	Found %:	C 46.28; H 3.99; N 4.66; Br 25.56
$C_{12}H_{10}O_4NBr$.	Calculated %:	C 46.15; H 3.20; N 4.5; Br 25.6

The oxazolinone (XIV) can be readily crystallized from ether, ethanol, methanol, and acetic anhydride in the form of colorless needles. It is readily soluble in chloroform and dioxan, has limited solubility in ether, and is insoluble in water. It is stable to the action of alkalis. An ethereal solution of (XIV) remains unchanged after being shaken with 0.5 N NaOH for six hours. When, however, the substance was heated with 0.5 N NaOH at 80°, decomposition occurred; acidification did not give a precipitate of the corresponding acid, but treatment with a 0.5% solution of 2,4-dinitrophenylhydrazine in 2 N HCl yielded the 2,4-dinitrophenylhydrazone of (benzoyloxy)pyruvic acid, m.p. 168-170° (from alcohol), identical with the hydrazone (X).

When heated with 25% sulfuric acid, the oxazolinone (XIV) rapidly dissolved, and addition of a 0.5% solution of 2,4-dinitrophenylhydrazine in 2 N HCl yielded a precipitate of the 2,4-dinitrophenylhydrazone of (benzoyloxy)pyruvic acid, m.p. 168-173°, undepressed by admixture of the hydrazone (X). 4-Acetoxy-4-(bromomethyl)-2-phenyl-2-oxazolin-5-one gave the characteristic hydroxamic reaction for anhydrides (red coloration with hydroxylamine and ferric chloride). When kept for 1-2 months it decomposed with separation of acetic acid and formation of a resin of unknown composition.

4-Acetoxy-4-(chloromethyl)-2-phenyl-2-oxazolin-5-one (XV). A mixture of 9.5 g (0.05 mole) of 2-benzamidoacrylic acid and a solution of 7 g (100% excess) of chlorine in 70 ml of carbon tetrachloride was shaken, with cooling (temperature not above 20-25°) for 30 minutes. Acetic anhydride (50 ml) was then added, and the mixture was heated under reduced pressure at 60-65°, the oxazolinone (XV) being isolated in the way described for the oxazolinone (XII). The crystalline precipitate was filtered off and washed with a small amount of absolute ether. The product was 4.6 g of the oxazolinone (XV), melting with decomposition at 110° (from absolute ethanol). A further 4.5 g was isolated from the mother liquor, and the total yield of (XV) was 68%. The oxazolinone (XV) is very soluble in chloroform and ether, and it crystallizes from methanol, ethanol, and acetic anhydride in the form of colorless needles.

$C_{12}H_{10}O_4NCl$. Found %: C 53.4; H 3.96; Cl 13.29
Calculated %: C 53.9; H 3.74; Cl 13.5

Special experiments showed that, even when heated for a long time, 4-acetoxy-4-(chloromethyl)-2-phenyl-2-oxazolin-5-one is not converted into 4-(chloromethylene)-2-phenyl-2-oxazolin-5-one. When the oxazolinone (XV) was prepared from crystalline N-benzoyl-2,3-dichloroalanine, a 74% yield was obtained.

SUMMARY

1. The addition of halogen to 2-(acylamino)acrylic acids has yielded some previously unknown N-acyl-2,3-dihaloalanines, namely N-benzoyl-2,3-dibromoalanine, N-benzoyl-2,3-dichloroalanine, 2,3-dibromo-N-(phenylacetyl) alanine, 2,3-dichloro-N-(phenylacetyl)alanine, and N-(benzyloxycarbonyl)-2,3-dibromoalanine.

2. It has been shown that in presence of acetic anhydride 2,3-dibromo(and dichloro)-N-(phenylacetyl)alanines are readily converted into 2-benzyl-4-(halomethylene)-2-oxazolin-5-ones, whereas under the same conditions N-benzoyl-2,3-dibromo(and dichloro)alanines yield stable 4-acetoxy-4-(halomethyl)-2-phenyl-2-oxazolin-5-ones.

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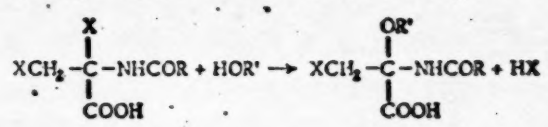
REACTIONS OF MERCAPTO AMINO ACIDS

COMMUNICATION 5. N-ACYL-3-HALO-2-HYDROXYALANINES AND THEIR DERIVATIVES

O. V. Kildisheva, M. G. Linkova, and I. L. Knunyants

In the preceding communication [1] we have described a method for the preparation of N-acyl-2,3-dihaloalanines and have shown that, whereas heating of N-benzoyl-2,3-dihaloalanines with acetic anhydride results in the formation of 4-acetoxy-4-(halomethyl)-2-phenyl-2-oxazolin-5-ones, 2,3-dihalo-N-(phenylacetyl)alanines yield 2-benzyl-4-(halomethylene)-2-oxazolin-5-ones under the same conditions. Further investigation of the properties of N-acyl-2,3-dihaloalanines has shown that they react readily with water and with alcohols, forming N-acyl-3-halo-2-hydroxyalanines (2-(acylamino)-3-halolactic acids) and N-acyl-2-alkoxy-3-haloalanines respectively (Table 1).

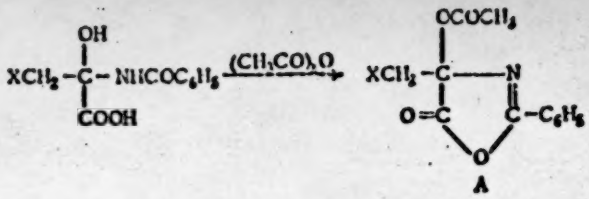


(I) X = Cl, R' = H, R = C_6H_5; (V) X = Cl, R' = H, R = $CH_2C_6H_5$;
(II) X = Cl, R' = CH_3, R = C_6H_5; (VI) X = Br, R' = H, R = $CH_2C_6H_5$;
(III) X = Cl, R' = C_2H_5, R = C_6H_5; (VII) X = Br, R' = C_2H_5, R = $CH_2C_6H_5$.
(IV) X = Br, R' = H, R = C_6H_5;

The most convenient method for the preparation of N-acyl-3-halo-2-hydroxyalanines is the treatment of N-acyl-2,3-dihaloalanines with an aqueous solution of an equimolecular proportion of sodium bicarbonate. When kept in a moist atmosphere and when treated with alkalis or acids, N-acyl-3-halo-2-hydroxyalanines are readily hydrolyzed with formation of ammonium halide. Alkaline solutions of these acids give a reddish-violet color with ferric chloride, a reaction that is characteristic of hydroxypyruvic acid. As in the case of N-acyl-2,3-dihaloalanines, the chloro acid is more stable than the bromo acid. Thus, when an N-acyl-3-bromo-2-hydroxyalanine is treated with an excess of sodium bicarbonate, or is allowed to stand in acid solution, decomposition readily occurs. Treatment of the acid hydrolyzates with 2,4-dinitrophenylhydrazine gives hydrazones identical with the 2,4-dinitrophenylhydrazones of (benzoyloxy)- and (phenylacetoxy)-pyruvic acids already prepared from N-acyl-2,3-dibromoalanines [1]. On the other hand, N-acyl-3-chloro-2-hydroxyalanines can be reprecipitated with acid from solutions of their sodium salts without decomposition. As a rule, both the bromo and the chloro acids are very soluble in organic solvents, but great losses are suffered when they are purified by recrystallization. When N-acyl-3-halo-2-hydroxyalanines are treated with not more than the theoretical amount of diazomethane, it is possible to obtain the corresponding methyl esters, but the yields are not high. When excess of diazomethane is used, the acylamino group is eliminated quantitatively as an amide.

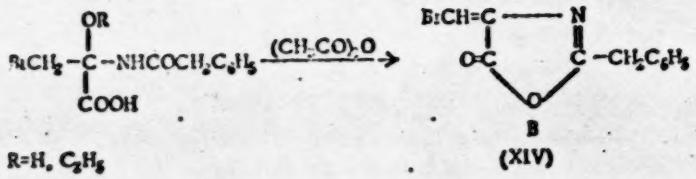
When treated with alcohols, N-acyl-2,3-dihaloalanines are immediately converted into N-acyl-2-alkoxy-3-haloalanines ((II), (III), and (VII) in the table). The latter compounds are more stable than the N-acyl-3-halo-2-hydroxyalanines: they are precipitated without decomposition from aqueous solutions of their sodium salts and can be crystallized unchanged from alcohols. They are converted quantitatively into the corresponding methyl esters by diazomethane ((X) and (XI) in the table). Further investigation has shown that heating of N-benzoyl-3-halo-2-hydroxyalanines with acetic anhydride results in the formation of the 4-acetoxy-4-(halomethyl)-2-phenyl-2-oxazolin-5-ones (XII) and (XIII), identical with the oxazolinones obtained by the action of acetic anhydride on N-benzoyl-2,3-dihaloalanines [1]. Under the same conditions, 3-halo-2-hydroxy(and alkoxy)-N-(phenylacetyl)alanines yield 2-benzyl-4-(halomethylene)-2-oxazolin-5-ones, identical with the oxazolinones obtained from 2,3-dihalo-N-(phenylacetyl)alanines: (See following page).

It has thus been established that, when acetic anhydride acts on N-acylalanines, different types (A and B) of oxazolinones are obtained, according to the identity of the acyl residue. Derivatives of N-banzoylalanine, such as N-benzoyl-2,3-dihalo- and N-benzoyl-3-halo-2-hydroxy-alanines, form only saturated oxazolinones of type A. On the other hand, derivatives of N-(phenylacetyl)alanine, whether they be 2,3-dihalo-, 3-halo-2-hydroxy-, or 2-alkoxy -3-halo-N-(phenylacetyl)alanines, form only unsaturated oxazolinones of type B. The question of whether or not the closure of the oxazolinone ring precedes the replacement of the 2-halo or 2-hydroxy by acetoxy was resolved



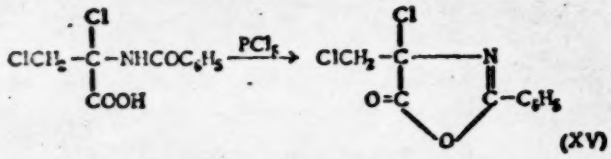
A

X=Cl (XII); X=Br (XIII)



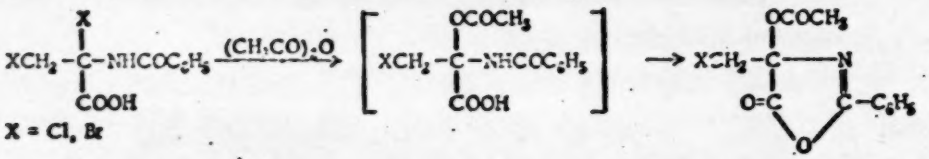
(XIV)

by a study of the behavior of 4-chloro-4-(chloromethyl)-2-phenyl-2-oxazolin-5-one (XV). This substance was readily prepared by the dehydration of N-benzoyl-2,3-dichloroalanine with the aid of phosphorus pentachloride:



(XV)

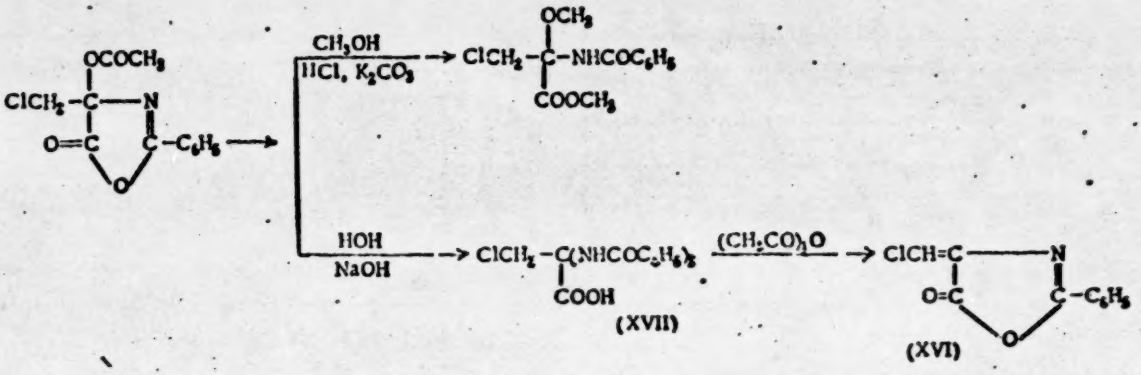
All attempts at converting the oxazolinone (XV) into 4-acetoxy-4-(chloromethyl)-2-phenyl-2-oxazolin-5-one or 4-(chloromethylene)-2-phenyl-2-oxazolin-5-one (XVI) were unsuccessful. Whereas N-acyl-2,3-dihaloalanines are readily converted by the action of a saturated solution of sodium bicarbonate into 3-halo-2-hydroxy compounds, the oxazolinone (XV) is not affected under these conditions. When treated for a longer time with water, or when treated with methanol, opening of the oxazolinone ring occurs, and only then does replacement of the 2-halogen occur with formation of N-benzoyl-3-chloro-2-hydroxyalanine (I), or the methyl ester of N-benzoyl-3-chloro-2-methoxyalanine (X). The formation of 4-acetoxy-4-(halomethyl)-2-phenyl-2-oxazolin-5-one from N-benzoyl-2,3-dihaloalanines is therefore preceded by replacement of 2-halo by acetoxy, after which dehydration to the corresponding oxazolinone occurs:



These first (halomethyl)oxazolinones were found to be fairly stable compounds; they can, for example, be melted without decomposition, kept for 2-3 months when moisture is excluded, and crystallized without difficulty from glacial acetic acid, acetic anhydride, and even alcohol [1]. 4-Acetoxy-4-(chloromethyl)-2-phenyl-2-oxazolin-5-one can be crystallized without change from a mixture of acetic anhydride and pyridine and is not affected when heated to 150°. Acid hydrolysis of 4-acetoxy-4-(halomethyl)-2-phenyl-2-oxazolin-5-ones gave (benzoyloxy)pyruvic acid, which was isolated in the form of its 2,4-dinitrophenylhydrazone, identical with the hydrazone obtained from the product of the acid hydrolysis of N-acyl-2,3-dihaloalanines.

Hydrolysis with aqueous sodium bicarbonate or methanolic 2 N NaOH gave 2,2-bis(benzamido)-3-chloropropionic acid (XVII), which melted with decomposition at 140-141°. Unlike N-benzoyl-3-chloro-2-hydroxyalanines and 2-alkoxy-N-benzoyl-3-chloroalanines, (XVII) is readily converted into the known 4-(chloromethylene)-2-phenyl-2-oxazolin-5-one (XVI) when heated with acetic anhydride: (See following page).

4-Acetoxy-4-(chloromethyl)-2-phenyl-2-oxazolin-5-one is hydrolyzed at room temperature by 80% acetic acid to N-benzoyl-3-chloro-2-hydroxyalanine. When it is treated with methanolic HCl or is heated with methanol in presence of very small amounts of potassium carbonate, the usual ester-formation reaction occurs, but, quite unexpectedly under these conditions, acetoxy is replaced by methoxy, and the product isolated is the methyl ester of N-benzoyl-3-chloro-2-methoxyalanine (X), identical with the ester obtained by the action of diazomethane on N-benzoyl-3-chloro-2-methoxyalanine.



EXPERIMENTAL

N-Benzoyl-3-chloro-2-hydroxyalanine (I). 1) N-Benzoyl-2,3-dichloroalanine (2.62 g, i.e. 0.01 mole) was vigorously agitated with a solution of 0.84 g (0.01 mole) of sodium bicarbonate in 9 ml of water. After ten minutes the precipitate formed was filtered off, washed with cold water, and dried over phosphoric oxide in a vacuum desiccator. The yield of N-benzoyl-3-chloro-2-hydroxyalanine (I), m.p. 111-114°, was 1.5 g (69%). The purification of the acid (I) by recrystallization from dichloroethane could be achieved only at the expense of great losses; m.p. 120-121° with a little decomposition.

	Found %:	C 49.2; H 4.07; N 5.47; Cl 14.14
$C_{10}H_{10}O_4NCl$.	Calculated %:	C 49.2; H 4.1; N 5.7; Cl 14.15

N-Benzoyl-3-chloro-2-hydroxyalanine is considerably more stable than the corresponding bromo acid; thus it can be reprecipitated with acids from aqueous solutions of its salts almost without loss and can be kept unchanged for a longer time.

2) 4-Acetoxy-4-(chloromethyl)-2-phenyl-2-oxazolin-5-one (0.26 g, i.e. 0.001 mole) was pasted with 1 ml of 50% acetic acid and left for three days at room temperature. After two days almost all of the precipitate had gone into solution, and the newly precipitated crystalline substance was filtered off, washed with a small amount of water, and dried. The product was 0.1 g of N-benzoyl-3-chlor-2-hydroxyalanine, m.p. 108-111° (with some decomposition), undepressed by admixture of some of the acid prepared from the dichloro acid.

N-Benzoyl-3-chloro-2-methoxyalanine (II). N-Benzoyl-2,3-dichloroalanine (2.6 g, i.e. 0.01 mole) was pasted with 3.5 ml of absolute methanol. The acid dissolved with noticeable evolution of heat, and after one minute a new crystalline precipitate formed. It was filtered off, washed with ether, and dried. The product was 2.0 g (78%) of N-benzoyl-3-chloro-2-methoxyalanine (II), m.p. 147-149° with decomposition. The acid (II) was dissolved in a saturated solution of sodium bicarbonate, and the solution was extracted with ether and then acidified with 25% sulfuric acid. The substance so obtained melted at 152-153°, raised by recrystallization from methanol to 159-160° (with decomposition).

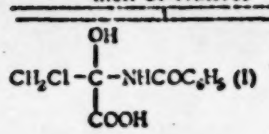
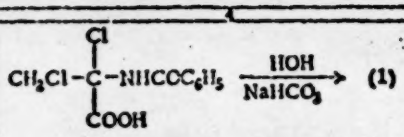
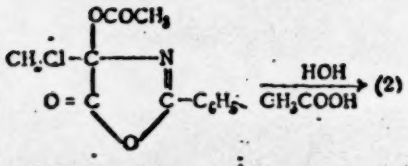
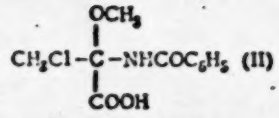
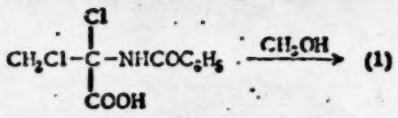
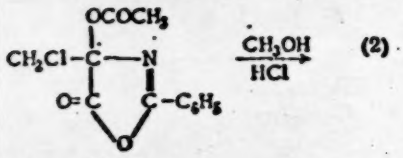
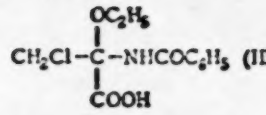
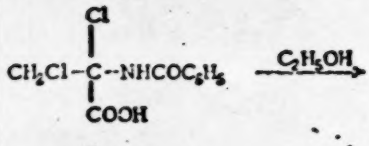
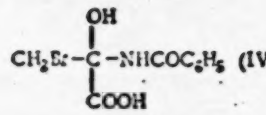
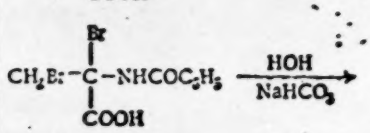
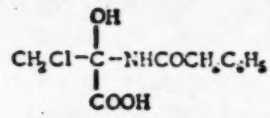
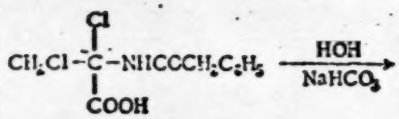
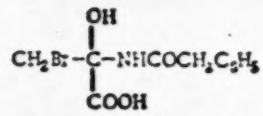
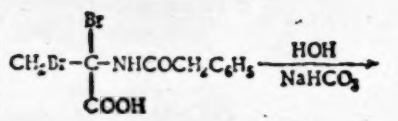
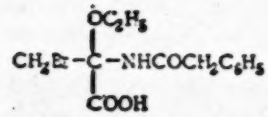
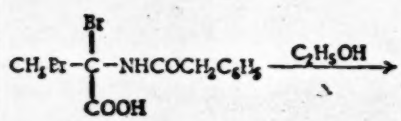
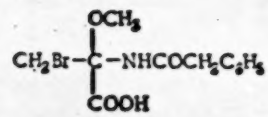
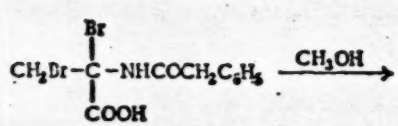
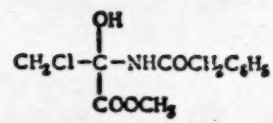
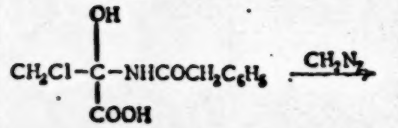
	Found %:	C 50.84; H 4.88; Cl 13.85; N 5.4
$C_{11}H_{12}O_4NCl$.	Calculated %:	C 51.2; H 4.66; Cl 13.87; N 5.43

N-Benzoyl-3-chloro-2-ethoxyalanine (III). N-Benzoyl-2,3-dichloro-alanine (2.6 g, i.e. 0.01 mole) was dissolved in 1 ml of absolute ethanol. Reaction occurred with evolution of an appreciable amount of heat. After two hours at 0-4°, a crystalline precipitate formed. It was filtered off, washed with a little water, and dried. The N-Benzoyl-3-chloro-2-ethoxyalanine obtained melted with decomposition at 115-117°. Some more was obtained by addition of ice water to the alcoholic mother liquor (total yield 80%). The acid (III) was reprecipitated by acids from its solution in aqueous sodium bicarbonate, but it formed as an oil, which solidified only after the addition of some of the crystalline acid (III). The acid (III) is very soluble in ethanol, methanol, and ether, but it is insoluble in water. It melts with decomposition at 117-118° after recrystallization from absolute ether or acetic anhydride (when the latter is used, the temperature must not rise above 50°).

	Found %:	C 52.88; H 5.43; Cl 13.4
$C_{12}H_{14}O_4NCl$	Calculated %:	C 53.04; H 5.15; Cl 13.07

N-Benzoyl-3-bromo-2-hydroxyalanine (IV). N-Benzoyl-2,3-dibromoalanine (12 g, i.e. 0.0032 mole) was agitated vigorously with a saturated solution of sodium bicarbonate (2.88 g, i.e. 0.032 mole, in 29 ml of water).

TABLE

N-Acyl-3-halo-2-hydroxyalanines and their derivatives	M.p. (°C)	Yield (%)	Method of preparation
 (I)	120-121	69	 (1)  (2)
 (II)	159-160	78	 (1)  (2)
 (III)	117-118	50	
 (IV)	105-106	94	
 (V)	105-106	70	
 (VI)	105-106	93	
 (VII)	126	70	
 (VIII)	125-126	–	
 (IX)	101-103	–	

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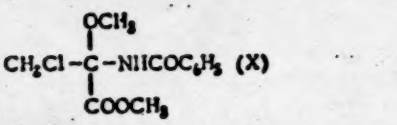
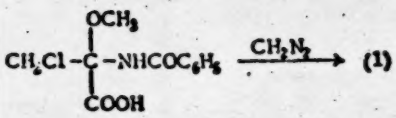
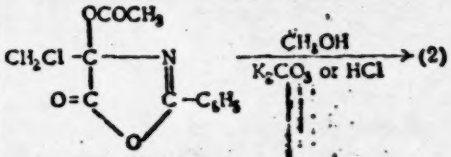
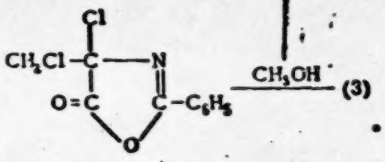
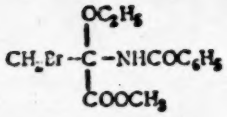
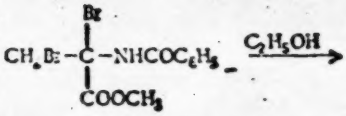
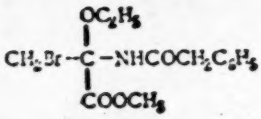
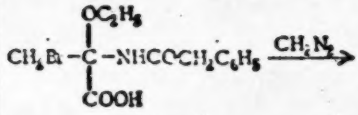
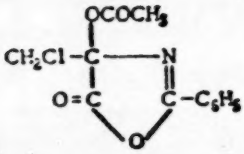
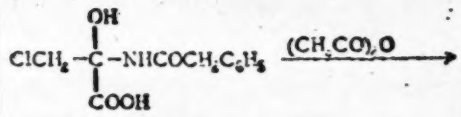
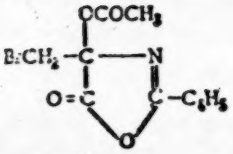
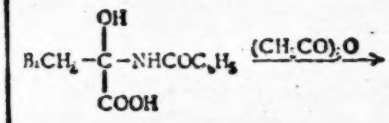
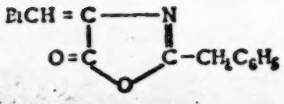
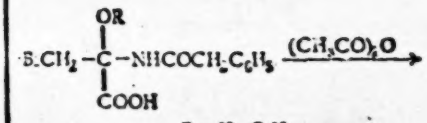
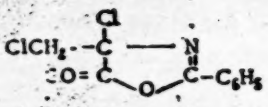
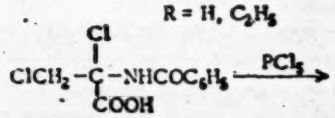
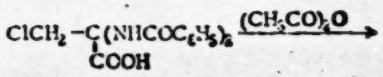
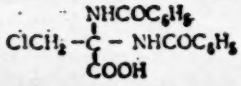
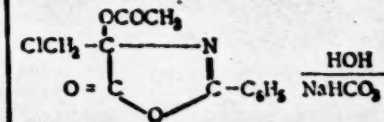
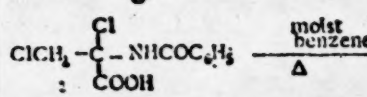
 (X)	105-106	quantitative	 (1)
		70	 (2)
			 (3)
	104-106	70	
 (XI)	97-98	60	
 (XII)	108-110		
 (XIII)	138		
 (XIV)	109-111 (decomp.)		 R = H, C_2H_5
 (XV)	70-74		
(XVI)	135-137	quantitative	
 (XVII)	140-141		 (1)  (2)

After 2-4 minutes the precipitate was filtered off, carefully washed with cold water, and dried over phosphoric oxide in a vacuum desiccator. The product was 8.7 g (91%) of N-benzoyl-3-bromo-2-hydroxyalanine, m.p. 105-106°.

	Found %:	C 41.93;	H 3.73;	Br 27.93
$C_{10}H_{10}O_4NBr$.	Calculated %:	C 41.66;	H 3.47;	Br 27.77

N-Benzoyl-3-bromo-2-hydroxyalanine is a colorless crystalline substance. It is decomposed by prolonged action of water or excess of sodium bicarbonate solution with formations of (benzoyloxy) pyruvic acid [1] and ammonium bromide. It is readily soluble in ethyl acetate, dioxan, and acetone, but poorly soluble in ether. Very great losses are suffered when it is crystallized from ethyl acetate.

3-Chloro-2-hydroxy-N-(phenylacetyl)alanine (V). 2,3-Dichloro-N-(phenylacetyl)alanine (2.76 g, i.e. 0.01 mole) was treated with a saturated solution of sodium bicarbonate (2 moles). The clear solution was acidified to Congo Red with 25% sulfuric acid. After ten minutes a crystalline precipitate formed. It was filtered off, washed with a small amount of water, and dried. The product was 1.8 g (70%) of 3-chloro-2-hydroxy-N-(phenylacetyl)alanine melting with some decomposition at 104-105°. The acid is readily soluble in alcohol and ethyl acetate. After recrystallization from ethyl acetate, in the course of which much of the substance is lost, it melts at 106-106.5°.

	Found %:	C 51.23;	H 4.73;	Cl 14.20
$C_{11}H_{12}O_4NCl$.	Calculated %:	C 51.26;	H 4.66;	Cl 13.8

3-Bromo-2-hydroxy-N-(phenylacetyl)alanine, (VI): a) 2,3-Dibromo-N-(phenylacetyl)alanine (3.65 g, was agitated vigorously with a saturated solution of sodium bicarbonate (0.84 g, i.e. 0.01 mole, in 8 ml of water); part of the dibromo acid went into solution. After 3-5 minutes the precipitate was filtered off, carefully washed with water, and dried over phosphoric oxide in a vacuum desiccator. The product was 2.7 g (93%) of 3-bromo-2-hydroxy-N-(phenylacetyl)alanine, melting with decomposition at 103-104°.

	Found %:	C 43.01;	H 4.38;	Br 26.35
$C_{11}H_{12}O_4NBr$	Calculated %:	C 43.7;	H 4.00;	Br 26.49

b) 2-(2-Phenylacetamido)acrylic acid (10 g, i.e. 0.05 mole) was brominated in the usual way. On the next day 40 ml of absolute ether was added to the reaction mixture, and heat was applied to effect solution. The undissolved residue was filtered off, and the filtrate was shaken vigorously while 2 ml of water was added. The mixture was left for 3-4 hours in a refrigerator, and the crystalline precipitate was then filtered off, washed with a small amount of chloroform, and dried over phosphoric oxide in a vacuum desiccator. The product was 7 g (50%) of 3-bromo-2-hydroxy-N-(phenylacetyl)alanine, m.p. 105-106°, undepressed by admixture of the substance obtained by method a).

3-Bromo-2-hydroxy-N-(phenylacetyl)alanine is an unstable compound. When treated with excess of alkali or acid it decomposes with formation of (phenylacetoxy)pyruvic acid and ammonium bromide. In titration with alkalis it behaves as a dibasic acid; the neutralization equivalent was calculated to be 151 and found to be 146. Silver bromide is quantitatively precipitated by 0.1 N $AgNO_3$. 3-Bromo-2-hydroxy-N-(phenylacetyl)alanine is very soluble in alcohol and ethyl acetate; it can be crystallized from dichloroethane or chloroform, but great losses occur. Treatment with acetic anhydride at 60-70° converts it into 2-benzyl-4-(bromomethylene)-2-oxazolin-5-one. When treated with ferric chloride, an alkaline solution of 3-bromo-2-hydroxy-N-(phenylacetyl)alanine immediately gives the reddish-violet color characteristic of hydroxypyruvic acid.

3-Bromo-2-ethoxy-N-(phenylacetyl)alanine (VII). 2,3-Dibromo-N-(phenylacetyl)alanine (3.65 g, i.e. 0.01 mole) was treated with 10 ml of absolute ethanol. The acid dissolved with evolution of an appreciable amount of heat, and in order to prevent decomposition the reaction mixture was cooled with ice water. After 1-2 minutes a crystalline precipitate was formed in the solution. The excess of alcohol was removed under reduced pressure at room temperature. The residue was dissolved in a saturated solution of sodium bicarbonate, and the solution was filtered and acidified to Congo Red with concentrated hydrochloric acid. An oil was precipitated. It rapidly solidified and was filtered off, carefully washed with water, and purified by repeated reprecipitation with acid from sodium bicarbonate solution. The product was 2.0 g (70%) of 3-bromo-2-ethoxy-N-(phenylacetyl)alanine, m.p. 126°.

	Found %:	C 47.52;	H 4.82;	Br 24.48
$C_{13}H_{16}O_4NBr$	Calculated %:	C 47.4;	H 4.55;	Br 24.3

3-Bromo-2-ethoxy-N-(phenylacetyl)alanine is a colorless crystalline substance. It is appreciably more stable than 2,3-dibromo-N-(phenylacetyl)alanine, but it is decomposed when kept for a long time in a moist atmosphere.

3-Bromo-2-methoxy-N-(phenylacetyl)alanine (VIII). The acid (VIII) was prepared similarly to the acid (VII), methanol being used in place of ethanol. The acid (VIII) melted with decomposition at 125-126° (from methanol).

	Found %:	C 45.16;	H 4.51;	Br 25.82
$C_{12}H_{14}O_4NBr$	Calculated %:	C 45.6;	H 4.42;	Br 25.4

Methyl Ester of 3-Chloro-2-hydroxy-N-(phenylacetyl)alanine (IX). 3-Chloro-2-hydroxy-N-(phenylacetyl) alanine (2.5 g) was suspended in 10 ml of absolute ether and treated with the calculated amount of an ethereal solution of diazomethane. When the addition was complete, the solution was rapidly filtered and ether was removed until crystallization began. The product was a mixture of the methyl ester of 3-chloro-2-hydroxy-N-(phenylacetyl)-alanine and 2-phenylacetamide. It was difficult to separate, but after numerous fractional crystallizations from a mixture of three parts of ether and one of ethyl acetate we succeeded in obtaining the methyl ester of 3-chloro-2-hydroxy-N-(phenylacetyl)alanine, m.p. 101-103°:

Found %: C 52,78; H 5,20; Cl 13,20
$C_{12}H_{14}O_4NCl$. Calculated %: C 53,04; H 5,15; Cl 13,07

and 2-phenylacetamide, m.p. 156-158°, undepressed by admixture of known 2-phenylacetamide.

Methyl Ester of N-Benzoyl-3-chloro-2-methoxyalanine (X). 1) N-Benzoyl-3-chloro-2-methoxyalanine (0.267 g, i.e. 0.001 mole) was mixed with 5 ml of absolute ether, and an ethereal solution of diazomethane was added in presence of a little methanol. After removal of a part of the ether, the methyl ester of N-benzoyl-3--chloro-2-methoxyalanine m.p. 103°, was obtained in almost quantitative yield. After recrystallization from absolute ether it melted at 105-106°.

Found %: C 52,84; H 5,2; Cl 12,33
$C_{12}H_{14}O_4NCl$ Calculated %: C 53,0; H 5,15; Cl 13,07

2) 4-Acetoxy-4-(chloromethyl)-2-phenyl-2-oxazolin-5-one (0.52 g, i.e. 0.002 mole) was mixed with 10 ml of methanol, 0.5 ml of a 10% solution of potassium carbonate was added, and the mixture was refluxed for 20 minutes. The mixture was then evaporated under reduced pressure to one-half of its original volume, 4 ml of water was added, and the mixture was set aside for 1-2 hours. The crystalline precipitate (0.36 g, i.e. 70%, of the methyl ester og N-benzoyl-3-chloro-2-methoxyalanine) was filtered off. Recrystallization from ether gave a product of m.p. 105-106°, undepressed by admixture of ester obtained by treatment of N-benzoyl-3-chloro-2-methoxyalanine with diazomethane.

3) 4-Acetoxy-4-(chloromethyl)-2-phenyl-2-oxazolin-5-one (2.67 g, i.e. 0.01 mole) was mixed with 10 ml of absolute methanol, and a catalytic amount of a saturated solution of hydrogen chloride in methanol was added. Reaction set in spontaneously with evolution of heat, and the oxazolinone went into solution. After partial evaporation of the methanol and cooling, a precipitate formed. It was filtered off, washed with water, and dried. The product was 2 g of a mixture of N-benzoyl-3-chloro-2-methoxyalanine and its methyl ester. In order to separate these the mixture was carefully ground with a 10% solution of sodium bicarbonate. The residue, filtered off, washed with water, and dried, was 1.3 g (50%) of the methyl ester of N-benzoyl-3-chloro-2-methoxyalanine, which melted, after recrystallization from methanol, at 104-105°. This ester was found to be identical with that obtained by the action of diazomethane on N-benzoyl-3-chloro-2-methoxyalanine. Careful acidification of the bicarbonate filtrate with N HCl under cooling with ice water yielded 0.4 g (15%) of an acid that melted with decomposition at 156-157° after recrystallization from methanol. There was no melting point depression in admixture with N-benzoyl-3-chloro-2-methoxyalanine obtained by the action of methanol on N-benzoyl-2,3-dichloroalanine.

Methyl Ester of N-Benzoyl-2,3-dibromoalanine. a) A mixture of 5.7 g of 2-benzamidoacrylic acid, 100 ml of methanol, 1 g of hydroquinone, 2 g of anhydrous sodium carbonate, and 8 g of dimethyl sulfate was refluxed for two hours. The mixture was cooled, and 200 ml of absolute ether was added. The precipitate that formed was filtered off, and the filtrate was evaporated under reduced pressure. The residue was again dissolved in absolute ether, and the solution was filtered and again evaporated. The yield of almost pure methyl 2-benzamidoacrylate was 3 g (50%). This ester could not be distilled, even in a vacuum; polymerization occurred at 150°. It was found that the 2-benzamidoacrylic ester absorbed the theoretical amount of bromine.

b) Methyl 2-benzamidoacrylate (1.9 g) was dissolved in 5 ml of absolute chloroform, and 16 ml of a 10% solution of bromine in chloroform was added in 5-ml portions. Reaction occurred with evolution of an appreciable amount of heat, and the bromine color rapidly disappeared. When addition of bromine was complete, the solution was evaporated under reduced pressure with exclusion of moisture. A theoretical yield was obtained of the methyl ester of N-benzoyl-2,3-dibromoalanine, m.p. 90-91° (from absolute ether). The ester is unstable and decomposes when kept in a moist atmosphere.

Found %: N 3,73; Br 42,3 (Volhard titration)
$C_{11}H_{11}O_3NBr_2$ Calculated %: N 3,83; Br 43,8

Methyl Ester of N-Benzoyl-3-bromo-2-ethoxyalanine. The methyl ester of N-benzoyl-2,3-dibromoalanine (0.36 g, i.e. 0.001 mole) was added to 1 ml of ethanol. The ester rapidly went into solution, and a crystalline precipitate of 0.2 g (70%) of the methyl ester of N-benzoyl-3-bromo-2-ethoxyalanine, m.p. 104-106°, was formed.

	Found %:	C 47.25;	H 4.44;	Br 24.02;	N 4.16
$C_{13}H_{16}O_4NBr$	Calculated %:	C 47.27;	H 4.31;	Br 24.24;	N 4.24

Methyl Ester of 3-Bromo-2-ethoxy-N-(phenylacetyl)alanine (XI). 3-Bromo-2-ethoxy-N-(phenylacetyl) alanine (0.5 g) was pasted with 2 ml of absolute ether, and an ethereal solution of diazomethane was added gradually. When the evolution of nitrogen ceased, the solution was filtered and placed in a refrigerator. A crystalline precipitate appeared after 10-15 minutes and was filtered off, washed with a small amount of absolute ether, and dried over phosphoric oxide in a vacuum desiccator. The product was 0.3 g of the methyl ester of 3-bromo-2-ethoxy -N--(phenylacetyl)alanine, m.p. 97-98°.

	Found %:	C 48.9;	H 5.36;	Br 22.85
$C_{14}H_{18}NO_4Br$	Calculated %:	C 48.8;	H 5.23;	Br 23.2

4-Acetoxy-4-(chloromethyl)-2-phenyl-2-oxazolin-5-one (XII). A mixture of 2.25 g (0.01 mole) of N-benzoyl-3-chloro-2-hydroxyalanine and 5 ml of acetic anhydride was heated at 70-80° for ten minutes. The acetic anhydride was distilled off at 10 mm residual pressure, and the residue was washed with ether. The product was 1.4 g (50%) of 4-acetoxy-4-(chloromethyl)-2-phenyl-2-oxazolin-5-one, m.p. 107-108° (from absolute alcohol). A mixture test with a sample prepared from N-benzoyl-2,3-dichloroalanine showed no depression.

The oxazolinone (XII) (0.267 g, i.e. 0.001 mole) was treated at 40° with a mixture of 0.2 g of acetic anhydride and 0.2 g of pyridine. The clear solution was set aside overnight, and on the next day a colorless crystalline precipitate appeared in the dark-red solution. The precipitate was filtered off and found to be unchanged oxazolinone (XII), m.p. 108-109°. All attempts at converting the oxazolinone (XII) into 4-(chloromethylene)-2-phenyl-2-oxazolin-5-one (XVI) were unsuccessful. It was found also that the oxazolinone (XII) was unaffected when heated to 150°.

4-Acetoxy-4-(bromomethyl)-2-phenyl-2-oxazolin-5-one (XIII). A mixture of 2.7 g (0.01 mole) of N-benzoyl-3-bromo-2-hydroxyalanine and 5 ml of acetic anhydride was heated for five minutes at 70-80°. The solution was poured into ice water, and the precipitate that formed was repeatedly washed with bicarbonate solution, and was then washed with water and dried over phosphoric oxide in a vacuum desiccator. The product was 1.3 g (41%) of 4-acetoxy-4-(bromomethyl)-2-phenyl-2-oxazolin-5-one, which melted, after recrystallization from absolute alcohol, at 134-135°. A mixture test with a sample prepared from N-benzoyl-2,3-dibromoalanine showed no depression.

2-Benzyl-4-(bromomethylene)-2-oxazolin-5-one (XIV). 1) A mixture of 2.84 g (0.01 mole) of 3-bromo-2--hydroxy-N-(phenylacetyl)alanine (m.p. 105-106°) and 5 ml of acetic anhydride was heated for 15 minutes at 60-65°. The orange-yellow solution was cooled and poured into three times its volume of ice water. A semisolid precipitate formed, and it was separated, washed first with a saturated solution of sodium bicarbonate and then with water, and dried over phosphoric oxide in a vacuum desiccator. The product was 0.5 g (18.8%) of 2-benzyl-4-(bromomethylene) -2-oxazolin-5-one, melting at 101° with decomposition. After being purified as already described [1], it melted at 106-107°. A mixture test with a sample prepared from 2,3-dibromo-N-(phenylacetyl)alanine showed no depression.

	Found %:	C 49.35;	H 3.28;	Br 30.09
$C_{11}H_9O_2NBr_2$	Calculated %:	C 49.62;	H 3.00;	Br 30.08

2) A mixture of 3.29 g (0.01mole) of 3-bromo-2-ethoxy-N-(phenylacetyl)alanine and 20 ml of acetic anhydride was heated for 30 minutes at 60-70°, and acetic anhydride was then removedunder reduced pressure until crystallization began. The crystalline precipitate was pasted with a small amount of absolute ether, and the residue was filtered off and washed with a little ether. The product was 1.5 g (56%) of the oxazolinone (XIV), melting with decomposition at 109-111°. A mixture test with a sample prepared from 2,3-dibromo-N-(phenylacetyl)alanine showed no depression.

4-Chloro-4-(chloromethyl)-2-phenyl-2-oxazolin-5-one (XV). N-Benzoyl-2,3-dichloroalanine (2.62 g, i.e. 0.01 mole) was suspended in 20 ml of absolute benzene, and the mixture was boiled with 2.1 g (0.01 mole) of phosphorus pentachloride for two hours. The mixture was then evaporated to dryness under reduced pressure. The residue was dissolved in a little benzene, and petroleum ether was added. A resinous precipitate formed and was separated; solvent was removed in a vacuum. The product was 1.8 g of 4-chloro-4-(chloromethyl)-2-phenyl-2-oxazolin-5-one (XV), m.p. 70-74°. It was not found possible to purify the oxazolinone (XV) by crystallization. It is readily soluble in benzene and ether, and moderately soluble in petroleum ether.

	Found %:	C 49.35;	H 3.45	
$C_{10}H_7O_2NCl_2$	Calculated %:	C 49.18;	H 2.86	

This substance reacts with water and with methanol even at room temperature with formation of N-benzoyl-3-chloro-2-hydroxyalanine and the methyl ester of N-benzoyl-3-chloro-2-methoxyalanine respectively. These products showed no depression in mixture tests with samples prepared by other methods. The oxazolinone (XV) is not affected by long boiling in benzene (no elimination of HCl occurs), and it is unaffected also when washed with a saturated solution of sodium bicarbonate.

2,2-Bis(benzamido)-3-chloropropionic Acid (XVII). 4-Acetoxy-4-(chloromethyl)-2-phenyl-2-oxazolin-5-one (0.6 g, i.e. 0.002 mole) was heated at 80° with a saturated solution of sodium bicarbonate. The solution was cooled and the precipitate present was filtered off (0.1 g of benzamide, giving no melting point depression in a mixture test with known benzamide). The filtrate was acidified to Congo Red with 25% sulfuric acid, and an oil was precipitated which gradually solidified. The precipitate was filtered off, washed with cold water, and dried over phosphoric oxide in a vacuum desiccator. The product was 0.15 g of 2,2-bis(benzamido)-3-chloropropionic acid (XVII), m.p. 140-141° (from dichloroethane).

	Found %:	C 58.86; H 4.29; N 7.78; Cl 9.87
$C_{17}H_{15}O_4N_2Cl$	Calculated %:	C 58.87; H 4.33; N 8.01; Cl 10.24

The acid (XVII) is readily soluble in alcohol and benzene, and can be crystallized from hot water. When heated with acetic anhydride at 60-70°, it immediately gives benzonitrile and 4-(chloromethylene)-2-phenyl-2-oxazolin-5-one (XVI), identical with the 4-(chloromethylene)-2-phenyl-2-oxazolin-5-one prepared by another method. The acid mother liquor that remained after isolation of the acid (XVII) was treated with a 0.5% solution of 2,4-dinitrophenylhydrazine in 2 N HCl, and 0.10 g of the 2,4-dinitrophenylhydrazone of (benzoyloxy)pyruvic acid was obtained. This melted at 168-171° (from alcohol) and was identical with the hydrazone obtained from (benzoyloxy)pyruvic acid.

SUMMARY

1. It has been shown that N-acyl-2,3-dihalogenalanines readily exchange their 2-halogens for hydroxyl, alkoxyl, acetoxy, and other groups.

2. It has been shown that in the presence of acetic anhydride 3-halo-2-hydroxy-N-(phenylacetyl)alanines and 2-alkoxy-3-halo-N-(phenylacetyl)alanines are readily converted into 2-benzyl-4-(halomethylene)-2-oxazolin-5-ones.

3. When acetic anhydride acts upon N-benzoyl-3-chloro-2-hydroxyalanine, 4-acetoxy-4-(chloromethyl)-2-phenyl-2-oxazolin-5-one is formed; whereas when it acts on 2,2-bis(benzamido)-3-chloropropionic acid, the product is 4-(chloromethylene)-2-phenyl-2-oxazolin-5-one.

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N.D. Zelinsky Institute of Organic Chemistry of the USSR Academy of Sciences

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[1] O.V. Kildisheva, L. P. Rastelkene, and I. L. Knunyants, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1955, No. 2, 260.*

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* See Consultants Bureau Translation, p. 231.

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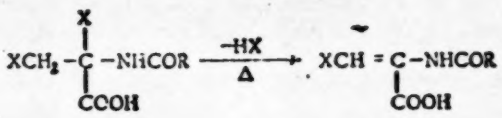
REACTIONS OF MERCAPTO AMINO ACIDS

COMMUNICATION 6. 2-ACYLAMINO-3-HALOACRYLIC ACIDS AND THEIR DERIVATIVES

O. V. Kildisheva, M. G. Linkova, and I. L. Knunyants

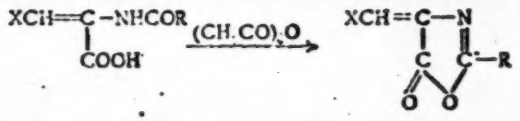
We have previously shown [1] that N-acyl-2,3-dihaloalanines are readily converted by the action of acetic anhydride into oxazolinones, having a side group that may be saturated or unsaturated depending on the identity of the N-acyl group. Further investigation of the properties of N-acyl-2,3-dihaloalanines has shown that, when they are heated in anhydrous solvents, hydrogen halide is readily eliminated and previously unknown 2-(acylamino)-3-haloacrylic acids (I, II, III, IV, in Table 1) are formed:



X = Br, Cl; R = C_6H_5, $CH_2C_6H_5$

2-(Acylamino)-3-haloacrylic acids are stable compounds, which can be readily crystallized from various solvents in the form of colorless needles, can be reprecipitated with acid from aqueous solutions of their salts, and react normally with diazomethane with formation of the corresponding methyl 2-(acylamino)-3-haloacrylates.

When treated with dehydration agents, 2-(acylamino)-3-haloacrylic acids (with the exception of 2-(benzyloxycarbonyl amino)-3-bromoacrylic acid) are converted into 2-aryl(or aralkyl)-4-(halomethylene)-2-oxazolin-5-ones (Table 2):



(VI) X = Cl, R = $CH_2C_6H_5$; (VII) X = Br, R = $CH_2C_6H_5$;

(VIII) X = Cl, R = C_6H_5; (IX) X = Br, R = C_6H_5;

Oxazolinones (VI) and (VII), prepared from 3-chloro- and 3-bromo-2-(2-phenylacetamido)acrylic acids, were found to be identical with the oxazolinones prepared by the action of acetic anhydride on 2,3-dichloro- and 2,3-dibromo-N-(phenylacetyl)alanines respectively [1]. Again, the oxazolinone (VIII) was found to be identical with the 4-(chloromethylene)-2-phenyl-2-oxazolin-5-one obtained previously be a method that left no doubt as to its structure, namely the action of thionyl chloride on 4-(hydroxymethylene)-2-phenyl-2-oxazolin-5-one [2]. The last compound was prepared by the action of acetic anhydride on an acetal of an (acylamino)malonaldehydic acid [3].

It is of interest that all of the synthesized 2-(acylamino)-3-haloacrylic acids give immediate intense colorations in presence of a carboxylic anhydride and pyridine or a pyridine base. For example, in presence of any anhydride (even an anhydride such as 2-benzyl-4-methyl-4-(2-phenylacetamido)-2-oxazolin-5-one) and a pyridine base, 3-bromo-2-(2-phenylacetamido)acrylic acid immediately gives a coloration, which is at first violet, but gradually becomes dark crimson.

Under the same conditions 2-benzamido-3-chloroacrylic acid gives a green coloration, which gradually changes to blue. These colors, which arise owing to the conversion of these acids into 2-aryl(or aralkyl)-4-(halomethylene-2-oxazolin-5-ones (which themselves give intense colorations with bases), enable 2-(acylamino)-3-haloacrylic acids to be used as sensitive reagents for the anhydride linkage.

When 2-(benzyloxycarbonylamino)-3-bromoacrylic acid is treated with acetic or trifluoroacetic anhydride, the internal anhydride of 3-bromo-2-(carboxyamino)acrylic acid (4-(bromomethylene)2,5-oxazolidinedione) (X) is formed; it melts with decomposition at 205-206° in a sealed capillary.

TABLE 1

2-(Acylamino)-3-halocrylic acid	M.p.(°C)	Method of preparation
$ClCH=C(COOH)-NHCOC_6H_5$ (I)	160-161 (decomp.)	$ClCH_2-C(Cl)(COOH)-NHCOC_6H_5 \xrightarrow[\Delta]{-HCl}$ (1) $ClCH=C-N$ / $O=C\ C-C_6H_5$ / $O \xrightarrow[NaHCO_3]{HOH}$ (2)
$BrCH=C(COOH)-NHCOC_6H_5$ (II)	154-156 (decomp.)	$BrCH_2-C(Br)(COOH)-NHCOC_6H_5 \xrightarrow[\Delta]{-HBr}$
$ClCH=C(COOH)-NHCOCH_2C_6H_5$ (III)	180-182 (decomp.)	$ClCH_2-C(Cl)(COOH)-NHCOCH_2C_6H_5 \xrightarrow[\Delta]{-HCl}$
$BrCH=C(COOH)-NHCOCH_2C_6H_5$ (IV)	174-175 (decomp.)	$BrCH_2-C(Br)(COOH)-NHCOCH_2C_6H_5 \xrightarrow[\Delta]{-HBr}$ (1) $BrCH=C-N$ / $O=C\ C-CH_2C_6H_5$ / $O \xrightarrow[NaOH]{HOH}$ (2)
$BrCH=C(COOH)-NHCOOCH_2C_6H_5$ (V)	163-164 (decomp.)	$BrCH_2-C(Br)(COOH)-NHCOOCH_2C_6H_5 \xrightarrow[\Delta]{-HBr}$

$$BrCH=C(COOH)-NHCO-OCH_2C_6H_5 \xrightarrow{(CH_3CO)_2O} BrCH=C(-NH-)C(=O)-O-C=O \quad (X)$$

Other dehydrating agents, such as phosphorus pentachloride, have the same action.

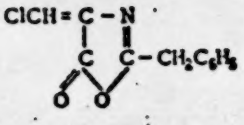
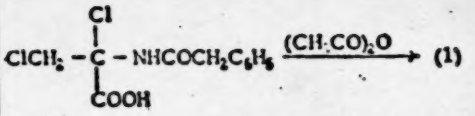
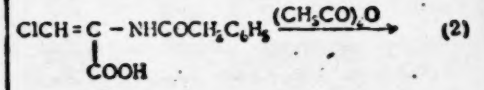
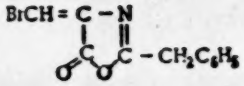
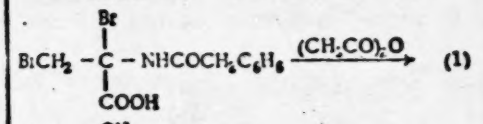
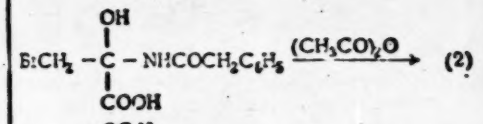
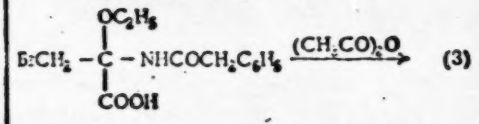
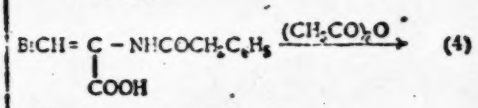
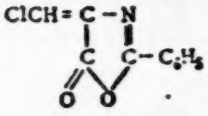
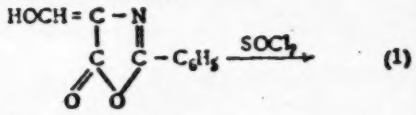
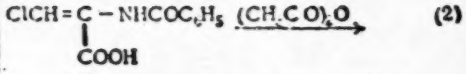
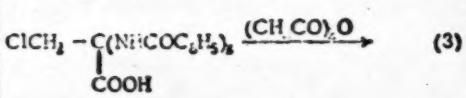
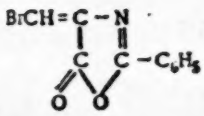
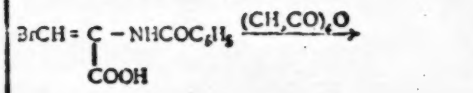
This internal anhydride is a representative of a new type of anhydride formed by unsaturated acylamino carboxylic acids.

Series 1 $BrCH=C(-N=)C(=O)-O-C-R_1$ $BrCH=C(-NH-)C(=O)-O-C=O$

Series 2 $CH_3-CH(-N=)C(=O)-O-C-R_1$ $CH_3-CH(-NH-)C(=O)-O-C=O$

A comparison of the properties of the derivatives of unsaturated acylamino carboxylic acids that we have synthesized (Series I) with those of the corresponding derivatives of saturated acylamino carboxylic acids (Series II) has shown that the compounds in the new series are incomparably more stable. The internal anhydride (X), for example, can be recrystallized uncharged from alcohols, whereas even at room temperature the internal anhydride of N-carboxyalanine is decarboxylated and converted into a macromolecular polypeptide [4, 5].

TABLE 2

2-Aryl(or Aralkyl)-4-(halomethylene)-2-oxazolin-5-one	M.p. (°C)	Method of preparation
 (VI)	114-115 (decomp.)	 (1)  (2)
 (VII)	112-114 (decomp.)	 (1)  (2)  (3)  (4)
 (VIII)	135-137 (decomp.)	 (1)  (2)  (3)
 (IX)	137 melts again at 189-192 (decomp.)	

EXPERIMENTAL

2-Benzamido-3-chloroacrylic Acid (I). A mixture of 2.6 g of N-benzoyl-2,3-dichloroalanine and 200 ml of absolute benzene was boiled for 40-50 minutes, and then cooled. The crystalline precipitate was filtered off, and then washed, first with a little dry benzene, and then with absolute ether. The product was 1.1 g (50%) of 2-benzamido-3-chloroacrylic acid, melting with decomposition at 160-161° (from absolute alcohol). In a mixture test with a sample of the acid prepared from 4-(chloromethylene)-2-phenyl-2-oxazolin-5-one there was no depression.

2-Benzamido-3-chloroacrylic acid is readily crystallized from acetic anhydride. When heating with acetic anhydride is prolonged, ready cyclization occurs with formation of the known 4-(chloromethylene)-2-phenyl-2-oxazolin-5-one, m.p. 135-137°. When it is heated in a moist solvent a by-product of the reaction is 2,2-bis(benzamido)-3-chloropropionic acid, m.p. 140-141° (from absolute alcohol), identical with the acid obtained by hydrolysis of 4-acetoxy-4-(chloromethyl)-2-phenyl-2-oxazolin-5-one [6].

Methyl 2-Benzamido-3-chloroacrylate. 2-Benzamido-3-chloroacrylic acid (2.2 g, i.e. 0.01 mole) was suspended in 25 ml of absolute ether and treated with an ethereal solution of diazomethane until nitrogen ceased to be evolved. The almost clear solution was filtered, and ether was evaporated until crystallization began. The product was 1.5 g (62.5%) of methyl 2-benzamido-3-chloroacrylate, m.p. 86-87°, raised to 93-94° by recrystallization from petroleum ether or 50% methanol. A mixture test with methyl 2-benzamido-3-chloroacrylate prepared by another method showed no depression.

2-Benzamido-3-bromoacrylic Acid (II). A mixture of 10 g (0.03 mole) of N-benzoyl-2,3-dibromoalanine and 500 ml of benzene was boiled for two hours with exclusion of moisture and with simultaneous distillation of benzene and hydrogen bromide. The reddish-brown solution was cooled and extracted with a saturated solution of sodium bicarbonate. The alkaline solution was extracted with a little ether and then acidified to Congo Red with concentrated hydrochloric acid. An oil separated, and after a few minutes it solidified and was filtered off. It was washed with cold water and dried over phosphoric oxide in a vacuum desiccator. The product was 1.7 g (22%) of 2-benzamido-3-bromoacrylic acid, melting with decomposition at 155-156° (from alcohol).

	Found %:	C 44.10; H 3.16; Br 29.22
$C_{10}H_8O_3NBr$.	Calculated %:	C 44.28; H 2.95; Br 29.5

2-Benzamido-3-bromoacrylic acid is readily soluble in acetone and alcohol; it is less soluble in ethyl acetate, and almost insoluble in benzene, ether, and cold acetic anhydride. When heated with acetic anhydride it is converted into 4-(bromomethylene)-2-phenyl-2-oxazolin-5-one. The acid (II) is reprecipitated unchanged by acids from the aqueous solutions of its salts.

3-Chloro-2-(2-phenylacetamido)acrylic Acid (III). 1) 2,3-Dichloro-N-(phenylacetyl)alanine (2.76 g, i.e. 0.01 mole) was suspended in 200 ml of benzene, and the mixture was boiled with exclusion of moisture for one hour. The mixture was cooled and the precipitate was filtered off, washed with a little water, dried, and crystallized from alcohol. The product was 1.2 g (50%) of 3-chloro-2-(2-phenylacetamido)acrylic acid, melting with decomposition at 180-182°.

	Found %:	C 54.44; H 4.25; Cl 15.0; N 5.91
$C_{11}H_{10}O_3NCl$.	Calculated %:	C 55.11; H 4.2; Cl 14.8; N 5.84

The acid is readily soluble in alcohol and ethyl acetate, less soluble in chloroform, and almost insoluble in benzene.

2) 2-Benzyl-4-(chloromethylene)-2-oxazolin-5-one (2.21 g, i.e. 0.01 mole) was heated at 50-60° with 0.5 N NaOH until the oxazolinone dissolved. The clear solution was cooled, extracted with ether, and acidified with concentrated hydrochloric acid. An oily precipitate formed. It solidified when rubbed, and was filtered off, washed with water, dried, and recrystallized from absolute alcohol. The product was 0.99 g (40%) of 3-chloro-2-(2-phenylacetamido)acrylic acid, m.p. 180-181°, undepressed by admixture of the acid obtained from 2,3-dichloro-N-(phenylacetyl)alanine.

3-Bromo-2-(2-phenylacetamido)acrylic Acid (IV). 1) 2-(2-Phenylacetamido)acrylic acid (20 g, i.e. 0.1 mole) was treated with a solution of 16 g (0.1 mole) of bromine in 160 ml of chloroform. On the next day 200 ml of absolute benzene was added, and the mixture was boiled with exclusion of moisture for three hours with simultaneous distillation of chloroform, benzene, and hydrogen bromide. The reddish-brown benzene solution was then extracted with a saturated solution of sodium bicarbonate, the alkaline solution was separated from the benzene, and residual benzene was removed by extraction with a little ether. The solution was acidified to Congo Red with concentrated hydrochloric acid, and the precipitate that formed was filtered off, washed with water, and dried over phosphoric oxide in a vacuum desiccator. The product was 20.5 g (72%) of 3-bromo-2-(2-phenylacetamido) acrylic acid melting with decomposition at 174-175° after recrystallization from absolute alcohol.

	Found %:	C 46.88; H 3.63; N 5.21
$C_{11}H_{10}O_3NBr$.	Calculated %:	C 46.47; H 3.52; N 4.93

3-Bromo-2-(2-phenylacetamido)acrylic acid is readily soluble in alcohol, acetone, and ethyl acetate; it has limited solubility in ether; and it is almost insoluble in water. It is reprecipitated unchanged by acids from aqueous solutions of its salts. It was found that an alkaline solution of 3-bromo-2-(2-phenylacetamido)acrylic acid did not give a violet color with ferric chloride, but after being warmed with 2 N NaOH for five minutes, ferric chloride gave the reddish-violet color characteristic for hydroxypyruvic acid. When the alkaline solution was acidified, 3-bromo-2-(2-phenylacetamido)acrylic acid was precipitated in almost quantitative yield. More prolonged heating (15 minutes) with 2 N NaOH resulted in decomposition, and 2-phenylacetamide was found among the decomposition products; it melted at 155-156°, and there was no depression in admixture with known 2-phenylacetamide.

2) 2-Benzyl-4-(bromomethylene)-2-oxazolin-5-one (11.8 g, i.e. 0.44 mole) was suspended in 200 ml of 0.5 N NaOH and heated at 70-80° until solution was complete (15 minutes). The solution was cooled, filtered, and acidified to Congo Red with concentrated hydrochloric acid. The precipitate was filtered off, washed with a little water, and dried over phosphoric oxide in a vacuum desiccator. The product was 4 g (32.5%) of 3-bromo-2-(2-phenylacetamido)acrylic acid, m.p. 172-173° (from acetone or alcohol), undepressed by admixture of a sample prepared from 2,3-dibromo-N-(phenylacetyl)alanine.

2-(Benzyloxycarbonylamino)-3-bromoacrylic Acid (V). N-(Benzyloxycarbonyl)-2,3-dibromoalanine (11 g, i.e. 0.05 mole) was treated with a solution of 8 g (0.05 mole) of bromine in 80 ml of chloroform. After one hour, the chloroform solution was evaporated to one-half of its original volume, 300 ml of absolute benzene was added, and the mixture was boiled with exclusion of moisture for four hours. It was then cooled, and the acid was isolated in the manner described for the acid (IV). The precipitate was filtered off, washed several times with cold water, and dried over phosphoric oxide in a vacuum desiccator. The product was 8.2 g (60%) of 2-(benzyloxycarbonylamino)-3-bromoacrylic acid, melting with decomposition at 163-164° (from aqueous alcohol).

2-(Benzyloxycarbonylamino)-3-bromoacrylic acid crystallizes in the form of colorless needles. It has limited solubility in benzene, ether, and chloroform, but is readily soluble in ethyl acetate and alcohol. It can be kept several months without change.

	Found %:	C 44.39; H 3.36; N 4.53
$C_{11}H_{10}O_4NBr$.	Calculated %:	C 44.0; H 3.33; N 4.66

Methyl 3-Bromo-2-(2-phenylacetamido)acrylate. 3-Bromo-2-(2-phenylacetamido)acrylic acid (5.68 g, i.e. 0.02 mole) was suspended in absolute ether and treated with an ethereal solution of diazomethane until evolution of nitrogen ceased. The whole of the acid went into solution. The solution was filtered rapidly and set aside at room temperature. After 10-15 minutes a crystalline precipitate began to form. The precipitate was filtered off and washed with a little ether. The product was 3.9 g (65%) of methyl 3-bromo-2-(2-phenylacetamido)acrylate, m.p. 90-91°. After recrystallization from absolute ether it melted at 100-101°.

	Found %:	C 48.19; H 4.07; N 4.85
$C_{12}H_{12}O_4NBr$.	Calculated %:	C 48.32; H 4.02; N 4.7

2-Benzyl-4-(chloromethylene)-2-oxazolin-5-one (VI). A mixture of 0.239 g (0.001 mole) of 3-chloro-2-(2-phenylacetamido)acrylic acid and 2 ml of acetic anhydride was heated at 80° for 15 minutes. The yellow solution was cooled and poured into ice water. The oil that was then precipitated solidified when rubbed. It was filtered off, washed with a saturated solution of sodium bicarbonate, dried, and recrystallized from ether. The product was 0.13 g (60%) of 2-benzyl-4-(chloromethylene)-2-oxazolin-5-one, melting with decomposition at 114-115°. In a mixture test with the oxazolinone prepared from 2,3-dichloro-N-(phenylacetyl)alanine there was no depression. With pyridine or a pyridine base the oxazolinone gave a characteristic dark-violet coloration.

2-Benzyl-4-(bromomethylene)-2-oxazolin-5-one (VII). A mixture of 2.8 g (0.01 mole) of 3-bromo-2-(2-phenylacetamido)acrylic acid and 10 ml of acetic anhydride was heated at 50-60° for 20 minutes. The acetic anhydride was distilled off at a residual pressure of 1 mm, and the residue was extracted with ether. The product was 2-benzyl-4-(bromomethylene)-2-oxazolin-5-one, m.p. 110-112°, undepressed by admixture of a sample prepared from 2,3-dibromo-N-(phenylacetyl)alanine.

4-(Chloromethylene)-2-phenyl-2-oxazolin-5-one (VIII). A mixture of 1.1 g (0.005 mole) of 2-benzamido-3-chloroacrylic acid and 10 ml of acetic anhydride was heated at 100° for 15 minutes. Acetic anhydride was then distilled off under reduced pressure until crystallization began. The crystalline precipitate was filtered off, washed first with a little ether and then with absolute alcohol, and dried over phosphoric oxide in a vacuum desiccator. The product was 0.82 g (80%) of 4-(chloromethylene)-2-phenyl-2-oxazolin-5-one, m.p. 135-137° (from acetic anhydride), undepressed by admixture of a sample of the oxazolinone obtained from 4-(hydroxymethylene)-2-phenyl-2-oxazolin-5-one [2].

4-(Bromomethylene)-2-phenyl-2-oxazolin-5-one (IX). A mixture of 0.6 g (0.002 mole) of 2-benzamido-3-bromoacrylic acid (m.p. 155-156°) and 2 ml of acetic anhydride was heated at 90-100° for five minutes. The mixture was then cooled and poured into ten times its volume of ice water. The yellow crystalline precipitate was filtered off, carefully washed with water, and dried over phosphoric oxide in a vacuum desiccator. The product was 0.3 g (53%) of 4-(bromomethylene)-2-phenyl-2-oxazolin-5-one, melting first at 137°, then resolidifying, and then melting again with decomposition at 189-192° (from a mixture of alcohol and chloroform).

	Found %:	C 47.45; H 2.61; Br 31.42
$C_{10}H_7O_2NBr$.	Calculated %:	C 47.6; H 2.33; Br 31.7

4-(Bromomethylene)-2-phenyl-2-oxazolin-5-one is very soluble in chloroform and ether, of limited solubility in alcohol, and may be crystallized from acetic anhydride. It gives a dark-green color with pyridine. With an ethereal solution of aniline an ethereal solution of 4-(bromomethylene)-2-phenyl-2-oxazolin-5-one gives 4-(anilinomethylene)-2-phenyl-2-oxazolin-5-one, m.p. 153-155° (from alcohol), undepressed by admixture of a sample of 4-(anilinomethylene)-2-phenyl-2-oxazolin-5-one prepared from known 4-(chloromethylene)-2-phenyl-2-oxazolin-5-one (152-155°).

Internal Anhydride of 3-Bromo-2-(carboxyamino)acrylic Acid (4-(Bromomethylene)-2,5-oxazolidinedione) (X). 2-(Benzyloxycarbonylamino)-3-bromoacrylic acid (3 g, i.e. 0.01 mole) was carefully mixed with 2.08 g (0.01 mole) of phosphorus pentachloride without permitting access of moisture. Reaction occurred with evolution of heat and vigorous evolution of hydrogen chloride. After 5-10 minutes the reaction mixture was diluted with a little absolute ether and filtered. The residue on the filter was washed with petroleum ether. An almost quantitative yield was obtained of the internal anhydride of 3-bromo-2-(carboxyamino)acrylic acid, melting with decomposition at 198-200° in a sealed capillary. The anhydride is readily soluble in ether, alcohol, and dioxan. When recrystallized from alcohol (dissolution temperature not above 55°), there are great losses; the recrystallized product melts with decomposition at 205-206° in a sealed capillary.

	Found %:	C 25.26; H 1.19; N 7.51; Br 41.62
$C_4H_2O_3NBr$.	Calculated %:	C 25.0; H 1.04; N 7.24; Br 41.6.

SUMMARY

1. It has been shown that 2-(acylamino)-3-haloacrylic acids can be prepared by the thermal elimination of hydrogen halide from N-acyl-2,3-dihaloalanines.

2. It has been shown that, by the action of acetic anhydride, 2-(acylamino)-3-haloacrylic acids are converted into 2-aryl(aralkyl)-4-(halomethylene)-2-oxazolin-5-ones.

3. By the action of dehydrating agents on 2-(benzyloxycarbonylamino)-3-bromoacrylic acid, the first representative of the class of unsaturated internal anhydrides of carboxyamino acids has been prepared, namely the internal anhydride of 3-bromo-2-(carboxyamino)acrylic acid.

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N. D. Zelinsky Institute of Organic Chemistry of the USSR Academy of Sciences

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* See Consultants Bureau Translation, p. 231.

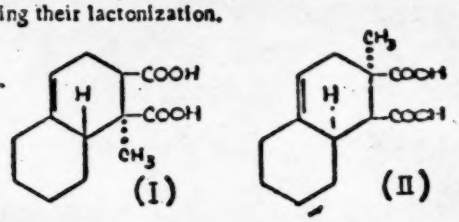
** See Consultants Bureau Translation, p. 241.

STEREOCHEMISTRY OF CYCLIC COMPOUNDS

COMMUNICATION 6. LACTONIZATION OF cis- AND trans-1,2,3,5,6,7,8,8a-OCTAHYDRO-1,2-NAPHTHALENEDICARBOXYLIC ACIDS

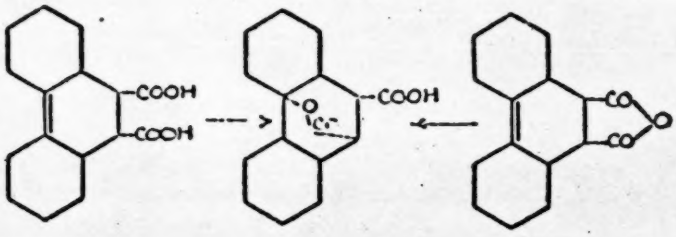
I. N. Nazarov, V. F. Kucherov, and V. M. Andreev

In the course of a study of the displacement of double bonds in the isomeric cis-1,2,3,5,6,7,8,8a-octahydro-methyl-1,2-naphthalenedicarboxylic acids (I) and (II) under acid conditions [1], we have made some interesting observations concerning their lactonization.

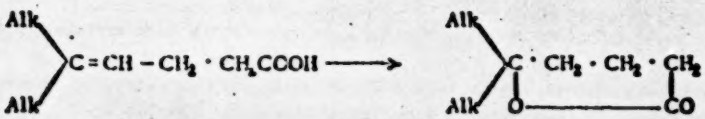


We have found that, when these acids are heated with a mixture of acetic acid and hydrogen chloride, they both give crystalline substances of the same composition $C_{15}H_{18}O_4$. These crystalline substances do not contain a double bond and have only one free carboxyl group: they do not decolorize a chloroform solution of bromine, they are not hydrogenated in acetic acid in presence of platinum oxide, they behave as monocarboxylic acids when titrated, and they give monoesters of composition $C_{14}H_{22}O_4$ with an ethereal solution of diazomethane. All of these facts indicate that, when the unsaturated cis-dicarboxylic acids (I) and (II) are treated with a mixture of acetic acid and hydrogen chloride, lactonization occurs with participation of one of the carboxyls and the double bond in the ring with formation of the corresponding saturated monocarboxylic lactone acids.

This tendency for unsaturated cyclic carboxylic acids to undergo lactonization has been noted several times before [2]. It has been examined in some detail by Adams and Gruber for the adduct obtained by the condensation of bicyclohexenyl with maleic anhydride [3]. They showed that this dibasic acid and its anhydride are readily cyclized by treatment with an alcoholic solution of hydrogen chloride with formation of a lactone acid or its ester:



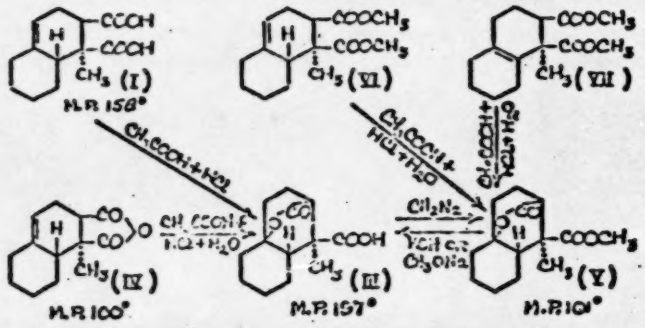
The authors ascribed a δ-lactone structure to the lactone acid, basing their view on the regularities previously found in a study of the lactonization of γ,δ-unsaturated fatty acids [4]. It was shown that, when these acids have alkyl groups on the δ-carbon, exclusive formation of δ-lactones occurs:



For the condensation of allylcyclohexanol with maleic anhydride, it has been inferred that the adduct is a δ-lactone from an examination of molecular models [5]. The tendency for γ, δ-unsaturated acids substituted

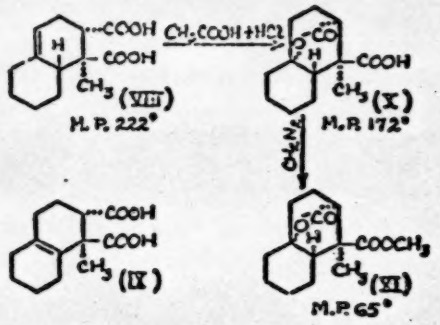
on the δ-carbon to give δ-lactones has been recently applied in the synthesis of ambreinolide [6]. The structural peculiarities of the unsaturated bicyclic cis-dicarboxylic acids (I) and (II) that we have selected for study have enabled us to investigate their lactonization in detail, to prove the structures of the lactones formed, and to investigate some of their reactions.

When the cis acid (I) was heated with acetic acid saturated with dry hydrogen chloride, the cis lactone acid (III), m.p. 197°, was readily formed in high yield. It was obtained also from the corresponding cis anhydride (IV). The cis lactone acid (III) behaved as a monocarboxylic acid in titration, and it was found that it does not contain a double bond. With diazomethane it gave the cis lactone ester (V), m.p. 101°. It was found that the lactone ester (V) can be obtained also by the partial hydrolysis in an acid medium of the cis diester (VI) or of the isomeric cis diester (VII), which has a double bond between the rings. These facts show that the lactone ring is always formed with the participation of the same carbon atom of the ring and the same carboxyl group.



The fact that the cis lactone ester (V) is not isomerized by treatment with sodium methoxide, but is only saponified with formation of the original cis lactone acid (III) in good yield, shows that it is the secondary carboxyl group at C − 2 that takes part in lactone formation. The formation of the cis lactone ester (V) from the cis diesters (VI) and (VII) also provides confirmation of this conclusion, since it is known that an esterified secondary carboxyl is more readily hydrolyzed than a tertiary ester grouping.

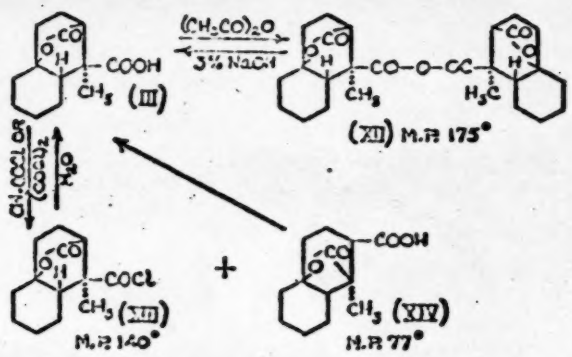
In order to resolve the question of which carbon atom of the ring (C − 4a or C − 8a) takes part in the lactonization and whether or not lactonization is accompanied by displacement of the double bond to the inter-ring position, we have studied the lactonization of the isomeric trans acids (VIII) and (IX). It was found that, under lactonization conditions, the trans acid (VIII) readily gives the trans-lactone acid (X), m.p. 172°, in good yield, and this is converted by diazomethane into the trans. lactone ester (XI), m.p. 65°. On the other hand, the trans acid (IX), which has an inter-ring double bond, was found to be quite incapable of lactonization, and when it was heated with acetic acid and hydrogen chloride, it was recovered unchanged.



These results show that the lactonization of the trans acids is not associated with a preliminary displacement of the double bond to the inter-ring position, so that it is the carbon in position 4a that takes part in the lactonization. Moreover, the same carbon atom C − 4a must take part also in the lactonization of the cis acid (I), since only then could the cis diesters (VI) and (VII) both form the same lactone ester (V)

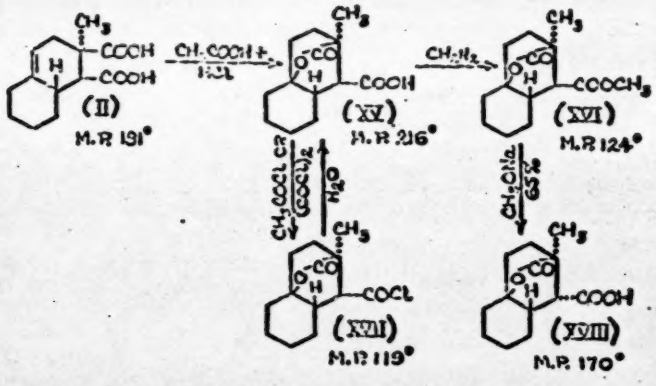
We have studied some of the chemical reactions of the cis lactone acid (III), and they show that the lactone ring is very stable in this compound. For example, when the cis lactone acid (III) is boiled with acetic

anhydride, it gives the anhydride (XII), m.p. 175°, the structure of which was proved by analysis and by determination of its molecular weight. Hydrolysis of this anhydride with weak alkali readily gives the original cis lactone acid (III). The reaction with acetyl chloride is more complex. From the mixture of the products of this reaction we have isolated two crystalline substances by fractional crystallization. One of these, m.p. 140°, corresponded in analysis to the acid chloride (XIII), and on hydrolysis with water it gave the original cis lactone acid (III) in quantitative yield. The same acid chloride (XIII) can be obtained in quantitative yield by the action of oxalyl chloride on the cis lactone acid (III), which provides final confirmation of its structure. The second crystalline product, m.p. 77°, corresponded by titration and analysis to an isomeric lactone acid $C_{11}H_{18}O_4$, and on standing it was gradually converted into the original cis lactone acid (III). This conversion goes to completion in presence of a little hydrogen chloride. It is possible that the lactone acid of m.p. 77° is the γ-lactone acid (XIV). Owing to the inaccessibility of this lactone acid, we were unable to investigate it in greater detail.

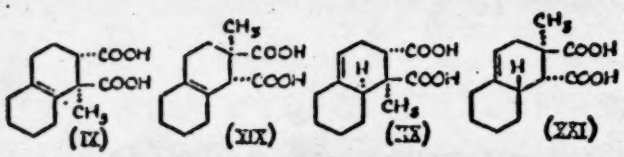


A study was made also of transformations of the cis acid (II) corresponding to those described above for the cis acid (I). When the cis acid (II) was heated with a mixture of acetic acid and hydrogen chloride, the stable cis lactone acid (XV), m.p. 216°, was readily formed in good yield. With diazomethane the lactone acid yielded the corresponding cis lactone ester (XVI), m.p. 124°, and with acetyl or oxalyl chloride it gave a good yield of the acid chloride (XVII), which could be hydrolyzed to the original cis lactone acid (XV). No by-products were isolated in this reaction.

In view of its δ-lactone structure, the cis lactone acid (XV) should be capable of undergoing isomerization when treated with sodium methoxide, and this is what is actually observed. It was found that the cis lactone ester (XVI), unlike the cis lactone ester (V), yielded a new lactone acid of m.p. 170° when isomerized with sodium methoxide. This substance, in accordance with its method of preparation, should be the trans lactone acid (XVIII).



Like the trans acid (IX), the trans acid (XIX) with an inter-ring double bond is not able to form lactones. The isomeric trans acids (XX) and (XXI) are also unable to give lactones, and they are peculiar also in being unable to undergo isomerization with displacement of the double bond to the inter-ring position [7].



The steric hindrances to the lactonization of the isomeric acids (IX), (XIX), (XX), and (XXI) may be in some measure explained with the aid of molecular models.

Molecular models in which the rings of the cis acids (I) and (II) are given the "chair" conformation indicate that the carboxyl at C-2 is spatially close to C-4a, thus facilitating the formation of a δ-lactone and making the formation of a γ-lactone with participation of the 1-carboxyl group difficult. For the cis diester (VII) with the double bond between the rings, which can be formed from the cis diester (VI) without strain, this approach is so close that the cis acid corresponding to it is almost nonexistent and, under conditions of partial hydrolysis, lactonization to the cis lactone ester (V) is bound to occur. In the trans acids (IX) and (XIX), which have inter-ring double bonds, the spatial disposition of the carboxyl groups is such that any sort of lactonization would be very difficult, and in fact no lactonization occurs.

Of the two epimeric trans acids (VIII) and (XX), which differ in the configuration of the hydrogen at C-8a, the trans acid (VIII), in which the substituent at C-2 is trans to the hydrogen at C-8a, can readily give a δ-lactone, whereas the trans acid (XX), in which the C-2 substituent is cis to the C-8a hydrogen, is not able to lactonize. This inference, which is in accord with the experimental results, is a further confirmation of the configurations that have been assigned to these acids [7] and to the trans acid (XXI), the spatial configuration of which should hinder lactonization. The molecular models show also that a displacement of the double bond into the inter-ring position will be extremely difficult in the trans acids (XX) and (XXI) and can be effected only by a complete rearrangement of the whole spatial configuration of the molecule.

EXPERIMENTAL

Lactonization of cis-1,2,3,5,6,7,8,8a-Octahydro-1-methyl-1,2-naphthalenedicarboxylic Acid (I)

a) A mixture of 10 g of the cis acid (I) and 100 ml of glacial acetic acid saturated with hydrogen chloride was heated for 90 minutes at 60°. The residue after removal of acetic acid under reduced pressure was a crystalline substance of m.p. 192-193.5°. Crystallization from a large volume of water yielded 8.2 g of the pure cis lactone acid (III) in the form of long glistening needles, m.p. 197-197.5°.

	Found %:	C 65.29; 65.23; H 7.81; 7.50
$C_{13}H_{18}O_4$.	Calculated %:	C 65.52; H 7.53
	Found M:	235.2; (titration with NaOH)
$C_{13}H_{18}O_4$.	Calculated M:	238.3

The cis lactone acid (III) does not decolorize a chloroform solution of bromine and is not hydrogenated in acetic acid in presence of platinum oxide.

b) A mixture of 0.5 g of the cis anhydride (IV), 5 ml of glacial acetic acid, and 1 ml of concentrated hydrochloric acid was heated at 60° for one hour. After removal of the acids under reduced pressure and crystallization of the residue from water, 0.25 g of the lactone acid (III) was isolated; it melted at 196-197°, and was identical with the substance obtained in the previous experiment. When dry hydrogen chloride was passed through a solution of the cis anhydride (IV) in absolute benzene for one hour at 60°, the anhydride was unaffected, being recovered unchanged when the benzene was distilled off.

c) A mixture of 0.8 g of the cis diester (VI) and 10 ml of a 40% solution of caustic potash was boiled for four hours. The mixture was acidified with hydrochloric acid, and the oil that then separated was extracted with ether. The ether was distilled off, and the liquid residue was boiled with 6 ml of 5% hydrochloric acid until solution was com-

plete. When the solution was cooled, 0.4 g of a crystalline substance of m.p. 190-192°, separated. Two recrystallizations from water yielded 0.3 g of the cis lactone acid (III), m.p. 196-197°, identical with that prepared in the preceding experiments.

The cis Lactone Ester (V)

a) A suspension of 3.1 g of the cis lactone acid (III) in ether was treated with an excess of an ethereal solution of diazomethane. After removal of ether, 3.2 g of crystals melting at 89-91° was obtained. Crystallization from a small amount of absolute ether yielded 2.8 g of pure cis lactone ester (V), m.p. 100-101°.

	Found %:	C 66.75; 66.84; H 8.10; 8.07
$C_{14}H_{26}O_4$.	Calculated %:	C 66.65; H 7.99

When the cis lactone ester (V) was hydrolyzed at the boil with 40% caustic potash, a good yield was obtained of the original cis lactone acid (III), m.p. 195-197° after recrystallization from water.

b) A solution prepared by dissolving 0.5 g of the cis diester (VI) in a mixture of 5 ml of glacial acetic acid and 1 ml of concentrated hydrochloric acid was set aside at room temperature overnight. The solvents were distilled off under reduced pressure, leaving a liquid residue, which crystallized when petroleum ether was added. Crystallization from ether yielded 0.35 g of pure cis lactone ester (V), m.p. 99-100°, identical with the substance obtained in the preceding experiment.

c) A mixture of 1.0 g of the cis diester (VII), 5 ml of glacial acetic acid, and 1 ml of concentrated hydrochloric acid was heated at 60° for two hours. The liquid residue remaining after removal of solvents at reduced pressure crystallized when treated with petroleum ether. The product was 0.45 g of crystals, melting at 94-96°. After crystallization from ether the melting point was 100-101°, undepressed by admixture of some of the cis lactone ester (V) obtained in the preceding experiment.

Attempt to Isomerize the cis Lactone Ester (V)

To a solution of 5 g of sodium in 125 ml of absolute methanol, 1.9 g of the cis lactone ester (V) was added, and the mixture was boiled for twelve hours. After removal of methanol under reduced pressure, the residue was dissolved in water, and the resulting solution was evaporated down in a porcelain dish on a water bath. The residue of salts was dissolved in the least possible amount of water, and the solution was acidified with hydrochloric acid. The oil that separated gradually solidified. The product (1.55 g) had a wide melting range (125-160°). Two crystallizations from ether yielded 0.85 g of a substance melting at 195-197°, which was found to be identical with the cis lactone acid (III). No other individual reaction products could be isolated.

Action of Acetic Anhydride on the cis Lactone Acid (III)

A mixture of 2.0 g of the cis lactone acid (III), m.p. 197-197.5°, and 20 ml of acetic anhydride was boiled for one hour. After removal of acetic anhydride under reduced pressure, a liquid reaction product was obtained, and this solidified when treated with benzene and petroleum ether. Crystallization from a mixture of benzene and petroleum ether yielded 1.2 g of a crystalline substance melting at 160-161°. After being recrystallized twice from a mixture of benzene and petroleum ether, the substance had a constant melting point of 174-175° and corresponded in analysis to the anhydride (XII).

	Found %:	C 63.32; 63.07; H 7.44; 7.58
$C_{28}H_{42}O_7$.	Calculated %:	C 63.10; H 7.48;
	Found M:	445.4 (cryoscopically in benzene)
$C_{28}H_{42}O_7$.	Calculated M:	458.5

A short boil with 3% caustic soda hydrolyzed the anhydride (XII) quantitatively to a substance of m.p. 195-196°, which was found to be identical with the cis lactone acid (III).

Action of Acetyl Chloride on the cis Lactone Acid (III)

The cis lactone acid (III) (1.5 g) was boiled with acetyl chloride (15 ml) for one hour. The crystalline reaction product obtained after removal of acetyl chloride was washed on the filter with a small amount of petroleum ether to which a few drops of diethyl ether had been added. The crystals obtained (1.2 g) melted at 109-121°, and when these were crystallized from ether, 0.6 g of a pure substance melting at 139-140° was obtained (fine glistening needles). This substance contained chlorine and corresponded in analysis to the acid chloride (XIII) of the cis lactone acid (III). The original cis lactone acid (III) was recovered quantitatively when this acid chloride was boiled with water.

	Found %:	C 61.36; 61.20; H 7.03; 6.82; Cl 13.77; 13.59
$C_{13}H_{17}O_3Cl$.	Calculated %:	C 60.81; H 6.68; Cl 13.81

The solution obtained by washing the crude reaction product was evaporated to low bulk, when 160 mg of crystals melting at 75.5-76.5° separated. After recrystallization from ether the substance melted at 76.5-77°, was free from chlorine, and corresponded by titration and elementary analysis to the isomeric cis lactone acid (XIV).

	Found %:	C 65.25; 65.30;	H 7.26; 7.37
$C_{13}H_{18}O_4$.	Calculated %:	C 65.52;	H 7.53
	Found M:	231.8 (titration with NaOH)	
$C_{13}H_{18}O_4$.	Calculated M:	238.3	

When kept, the cis lactone acid (XIV) was gradually converted into the cis lactone acid (III). This change occurred particularly readily when a little hydrogen chloride was present. Owing to its inaccessibility and instability, we were not able to make a more detailed study of the chemical properties of the cis lactone acid (XIV).

Acid Chloride (XIII) of the cis Lactone Acid (III)

Oxalyl chloride (0.5 ml) was added to a solution of 0.5 g of the cis lactone acid (III) in 5 ml of absolute benzene, and the mixture was heated at 50° for 2 hours 30 minutes. The residue remaining after removal of solvent crystallized when treated with petroleum ether. The product was 0.5 g of a substance melting at 138-139°. After recrystallization from ether it melted at 139-140°, and there was no depression in a mixture test with the acid chloride (XIII) prepared previously by the action of acetyl chloride on the cis lactone acid (III).

Lactonization of cis-1,2,3,5,6,7,8,8a-Octahydro-2-methyl-1,2-naphthalenedicarboxylic Acid (II)

A mixture of 1.0 g of the cis acid (II), m.p. 180-181°, and 10 ml of glacial acetic acid saturated with dry hydrogen chloride was heated at 60° for one hour. The acetic acid was driven off under reduced pressure, and, after crystallization from a small amount of water, the crystalline residue yielded 0.75 g of pure cis lactone acid (XV) in the form of fine needles melting at 216-216.5°.

	Found %:	C 65.74; 65.40;	H 7.58; 7.69
$C_{13}H_{18}O_4$.	Calculated %:	C 65.52;	H 7.53
	Found M:	230.9 (titration with NaOH)	
$C_{13}H_{18}C_4$.	Calculated M:	238.3	

The cis Lactone Ester (XVI)

The cis lactone acid (XV) of m.p. 215-216° (0.5 g) was treated in ether suspension with an excess of ethereal diazomethane. After removal of ether and treatment of the residue with petroleum ether, 0.45 g of the cis lactone ester (XVI), m.p. 119-121°, was obtained. After crystallization from ether it had a constant melting point of 123-124°.

	Found %:	C 66.87; 66.85;	H 7.91; 8.01
$C_{14}H_{20}O_4$.	Calculated %:	C 66.65;	H 7.99

When the cis lactone ester (XVI) was hydrolyzed with boiling 30% caustic potash, the original cis lactone acid (XV), m.p. 214-216°, was obtained in good yield.

Acid Chloride (XVII) of the cis Lactone Acid (XV)

A solution of 0.15 g of the cis lactone acid (XV) and 0.5 ml of oxalyl chloride in 2 ml of absolute benzene was heated at 50° for two hours. After removal of solvent, 170 mg of crystals melting at 118-120° were obtained, and recrystallization of these from ether yielded the pure acid chloride (XVII), m.p. 118-119°.

	Found %:	C 60.68; 60.66;	H 6.63; 6.69;	Cl 13.88; 13.90
$C_{12}H_{17}O_3Cl$.	Calculated %:	C 60.81;	H 6.68;	Cl 13.81

The same acid chloride (XVII) was the main product when the reaction was carried out with acetyl chloride. Hydrolysis of the acid chloride (XVII) with water gave a quantitative yield of the original cis lactone acid (XV).

The trans Lactone Acid (XVIII)

The cis lactone ester (XVI) of m.p. 123-124° (0.47 g) was added to a solution of 1.2 g of sodium in 35 ml of absolute methanol, and the mixture was boiled for 15 hours. The methanol was distilled off, 10 ml of water was added, and the solution was boiled for a further five hours. The mixture was evaporated in a porcelain dish, and the precipitate of salts was filtered off and dissolved in water. The solid obtained by acidification of this solution was crystallized twice from benzene, and 0.25 g of the trans lactone acid (XVIII), m.p. 169-170°, was obtained.

	Found %:	C 65.49; 65.59; H 7.67; 7.54
$C_{13}H_{18}O_4$.	Calculated %:	C 65.52; H 7.53
	Found M:	232.1 (titration with NaOH)
$C_{13}H_{18}O_4$.	Calculated M:	238.3

Lactonization of trans-1,2,3,5,6,7,8,8a-Octahydro-1-methyl-1,2-naphthalenedicarboxylic Acid (VIII)

The trans acid (VIII) of m.p. 221-222° (1.0 g) was heated at 40° for one hour with 10 ml of a saturated solution of dry hydrogen chloride in glacial acetic acid. Acetic acid was distilled off under reduced pressure, and the semisolid residue solidified when treated first with benzene and then with ether, these solvents being added to the residue and then removed by distillation. The product was washed on the filter with a mixture of two parts of petroleum ether and one of diethyl ether, and 0.82 g of a substance of m.p. 163-166° was obtained. After crystallization from a large volume of water the pure trans lactone acid (X) melted at 171-172°.

	Found %:	C 65.45; 65.55; H 7.63; 7.72
$C_{13}H_{18}O_4$.	Calculated %:	C 65.52; H 7.53
	Found M:	237.1 (titration with NaOH)
$C_{13}H_{18}O_4$.	Calculated M:	238.3

The trans Lactone Ester (XI)

The trans lactone acid (X) (0.4 g) was treated with ethereal diazomethane. The liquid reaction product obtained after removal of ether crystallized when treated with petroleum ether. The yield of the trans lactone ester (XI) was 0.4 g. It melted at 64-65.5° (64.5-65.5° after recrystallization from petroleum ether).

	Found %:	C 66.91; 66.87; H 8.06; 8.14
$C_{14}H_{20}O_4$.	Calculated %:	C 66.65; H 7.99

Hydrolysis of the trans lactone ester (XI) with 40% caustic potash gave the original trans lactone acid (X), m.p. 170-172°, in low yield.

Attempts to Lactonize the trans Acids (IX) and (XIX)

a) A mixture of 0.25 g of trans-1,2,3,4,5,6,7,8-octahydro-1-methyl-1,2-naphthalenedicarboxylic acid (IX), m.p. 170-171°, and 2.5 ml of glacial acetic acid saturated with dry hydrogen chloride was heated at 60° for one hour. The crystalline residue remaining after removal of acetic acid was crystallized from aqueous acetone and yielded 0.19 g of the original trans acid (IX), m.p. 169-170°.

b) A mixture of 0.15 g of trans-1,2,3,4,5,6,7,8-octahydro-2-methyl-1,2-naphthalenedicarboxylic acid (XIX), m.p. 173-174°, and 2 ml of glacial acetic acid saturated with dry hydrogen chloride was heated at 60° for 90 minutes. Acetic acid was removed under reduced pressure. Two crystallizations of the residue from a mixture of benzene and petroleum ether yielded 0.1 g of an acid of m.p. 171-173°, undepressed by admixture of some of the original trans acid (XIX).

Attempts to Lactonize the trans Acids (XX) and (XXI)

a) A mixture of 0.8 g of trans-1,2,3,5,6,7,8,8a-octahydro-1-methyl-1,2-naphthalenedicarboxylic acid (XX), m.p. 185-186°, and 8 ml of glacial acetic acid saturated with dry hydrogen chloride was heated at 60° for one hour. A thick oil remained after removal of acetic acid by distillation, and this partially crystallized when rubbed in presence of petroleum ether. The crystals were filtered off and washed with petroleum ether. Crystallization from water yielded 0.1 g of a crystalline substance, m.p. 169-171°, undepressed by admixture of the previously prepared trans lactone acid (X). The mother liquor, after treatment with a mixture of diethyl ether and petroleum ether, yielded 0.55 g of a substance that melted at 184-186° after crystallization from 30% aqueous methanol; it was found to be the original trans acid (XX).

b) A mixture of 0.17 g of trans-1,2,3,5,6,7,8,8a-octahydro-2-methyl-1,2-naphthalenedicarboxylic acid (XXI), m.p. 212-213°, and 2 ml of glacial acetic acid saturated with hydrogen chloride was heated at 60° for one hour. The residue remaining after removal of acetic acid under reduced pressure was crystallized twice from 40% aqueous acetone, and yielded 0.13 g of the original trans acid (XXI), m.p. 211-212°.

SUMMARY

1. A study has been made of the lactonization of the cis-1,2,3,5,6,7,8,8a-octahydromethyl-1,2-naphthalenedicarboxylic acids (I) and (II), and also of the cis diesters (VI) and (VII), and evidence relating to the structures of

the resulting cis lactone acids (III) and (XV) has been presented.

2. It has been shown that, of the epimeric trans acids (VIII) and (XX), only the trans acid (VIII) is capable of undergoing lactonization – a result in accord with the spatial configuration of (VIII). The trans acid (XX) and the trans acids (IX) and (XIX), which have inter-ring double bonds, are incapable of lactonization.

3. An examination of molecular models has provided an explanation of the experimentally observed steric hindrance to the lactonization of the trans-octahydromethyl-1,2-naphthalenedicarboxylic acids (IX), (XIX), and (XX).

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* See Consultants Bureau Translation, p. 67.
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STEREOCHEMISTRY OF CYCLIC COMPOUNDS

COMMUNICATION 7. GEOMETRIC ISOMERISM OF 4-METHYL-1,2-CYCLOHEXANEDICARBOXYLIC ACIDS

I. N. Nazarov and V. F. Kucherov

The establishment of the fact that, under normal conditions, the cyclohexane molecule exists in the "chair" form [1] makes it possible to obtain a more definite picture of the actual geometric configurations of cyclic compounds. The existence of the cyclohexane molecule in the chair form implies the presence in the molecule of six "equatorial" and six "polar" carbon-hydrogen bonds alternating among themselves. Correspondingly, in the molecule of a disubstituted cyclohexane, the substituents, irrespective of their structural arrangement, may be mutually disposed in three different ways, which may be described as equatorial-polar (e-p) (I), diequatorial (e-e) (II), and dipolar (p-p) (III).

(I) (II) (III)

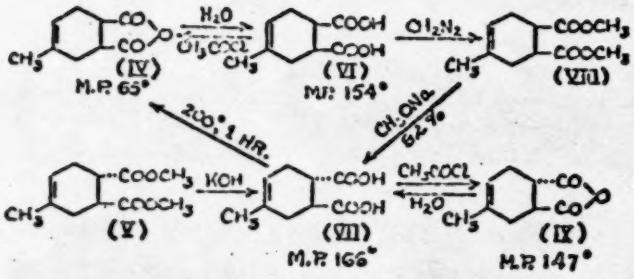
It is not difficult to see that the equatorial-polar arrangement of substituents will correspond to the cis-1,2-, trans-1,3-, and cis-1,4-isomers, whereas the other three isomers (trans-1,2-, cis-1,3-, and trans-1,4-isomers) can have either diequatorial or dipolar arrangements of substituents. Thermodynamic calculations for the isomeric dimethylcyclohexanes [2] have shown that the diequatorial arrangement of substituents is considerably more advantageous energetically than the dipolar arrangement. Correspondingly, under normal conditions the trans-1,2-, cis-1,3-, and trans-1,4-dimethylcyclohexanes exist only in the diequatorial forms. These conclusions were later confirmed in a study of the kinetics of the esterification of the isomeric cyclohexanedicarboxylic acids [3], and also in a study of the dissociation constants of various hydroxycyclohexanecarboxylic acids [4]. From dipole-moment measurements it has been proved quite rigorously that the trans-1,4-dichloro (and dibromo) cyclohexanes have the (e-e) disposition of substituents in the solid state [5]. Chemical confirmation of the diequatorial disposition of the carboxyl groups in trans-1,2-cyclohexanedicarboxylic acids is provided by the readiness with which they are dehydrated with formation of meso-trans anhydrides.

These conclusions concerning the higher stability of the equatorial disposition of substituents in disubstituted cyclohexanes have recently been extended with success to the elucidation of the stereochemistry of the complex polycyclic systems of steroids and polyterpenes [6].

The establishment of the absolute geometric configurations of cyclic compounds is one of the main problems of stereochemistry, and we therefore considered that it would be of interest to make a more detailed study of the stereochemistry of trisubstituted cyclohexanes. As a suitable subject for investigation we selected 4-methyl-1,2-cyclohexanedicarboxylic acid.

For the preparation of all of the four stereoisomers of this acid that are predicted by theory, the most convenient method was that based on the diene condensation of isoprene with maleic anhydride [7,8] and with fumaric ester [10], followed by hydrogenation of the resulting adducts. The chemical transformations of our starting materials may be presented as follows: (See top of following page).

When studying the hydrogenation of the anhydride of cis-4-methyl-4-cyclohexane-1,2-dicarboxylic acid (IV), Craig [8] found that a mixture of two isomers was formed (separated by crystallization in the form of the corresponding acids), and that one of these readily isomerized to the other when heated with dibutylaniline. Comparing these results with the stereochemical transformations of adducts obtained by the condensation of cis- and trans-piperylenes with maleic anhydride, Craig concluded that the isomer was trans-4-methyl-cis,cis-1,2-cyclohexanedicarboxylic acid.

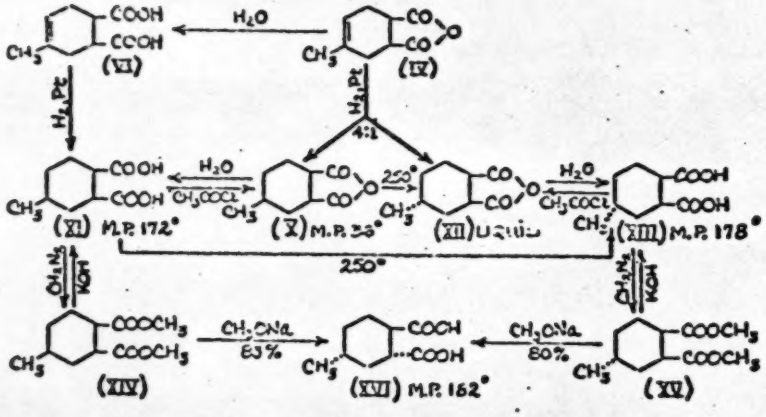


We have made a detailed study of the hydrogenation of the cis and trans anhydrides (IV) and (IX), and also of the corresponding acids (VI) and (VII).

It was found that hydrogenation of the cis anhydride (IV) in benzene solution over platinum oxide yielded a mixture of crystalline and liquid saturated anhydrides (X) and (XII) in the proportions of 4 : 1 approximately. The crystalline anhydride (X), m.p. 36°, was hydrolyzed by water to the saturated cis dicarboxylic acid (XI), m.p. 172-172.5°, whereas the liquid anhydride (XII) yielded the isomeric cis dicarboxylic acid (XIII), m.p. 178-179°. Both of these isomeric acids correspond to the acids obtained by Craig, and in admixture they show a great depression in melting point. Hydrogenation of the cis acid (VI) over platinum oxide in methanol was found to proceed much more selectively, and the main product was the acid (XI) with only a slight amount of the isomeric acid (XIII) as impurity.

This interesting fact is an indication that the screening of the double bond in the cis acid (VI), which is effected by the two cis-ortho carboxyl groups, is more effective than that of the double bond in the anhydride (IV), in which it is effected by the cis anhydride grouping. For this reason the addition of hydrogen to the cis acid (VI) occurs almost exclusively from the side opposite to the carboxyl groups with formation of the saturated acid (XI), in which the methyl group is on the same side as the carboxyl groups. This result is in full accord with data that indicate that catalytic hydrogenation is a reaction of cis addition of hydrogen.

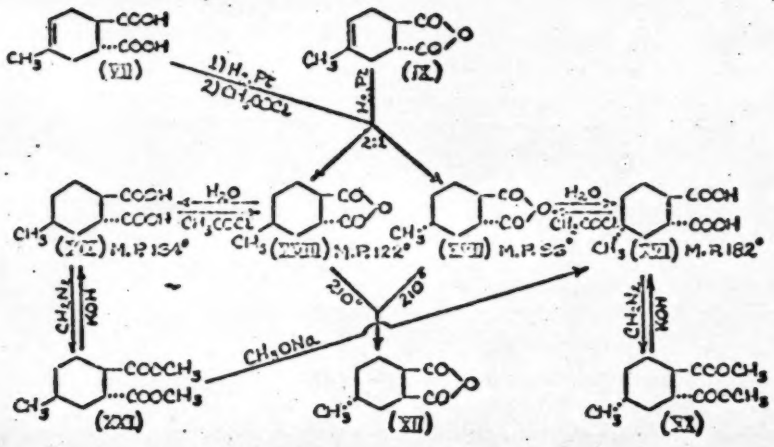
A study of the thermal stabilities of the isomeric cis dicarboxylic acids (XI) and (XIII) and of their anhydrides (X) and (XII) has shown that, when the acid (XI), or the corresponding anhydride (X), is heated for a short time at 240-250°, a mixture of isomeric anhydrides (X) and (XII) is formed, with a great predominance of the latter. When this mixture is hydrolyzed, the pure cis dicarboxylic acid (XIII) can be isolated in good yield by crystallization from aqueous methanol. These results indicate the high stability of the cis acid (XIII), as compared with the isomeric cis acid (XI), and are in accord with the results obtained for the adducts formed by cis- and trans-piperylenes with maleic anhydride [8].



When treated with ethereal diazomethane, the isomeric cis dicarboxylic acids (XI) and (XIII) yielded the corresponding cis diesters (XIV) and (XV). Isomerization of these cis diesters in presence of sodium methoxide yielded, in each case, the trans acid (XVI), m.p. 181-182°, which was converted by acetyl chloride into the trans anhydride (XVII), m.p. 96-97°. This fact indicates that in the isomerization of the diesters (XIV) and (XV) in presence of sodium methoxide, different carbon atoms are affected. Isomerization of the diester (XIV) is accompanied by rearrangement of the bonds at C-1, whereas the diester (XV) undergoes a like change at C-2, the result being that the same trans acid (XVI) is formed.

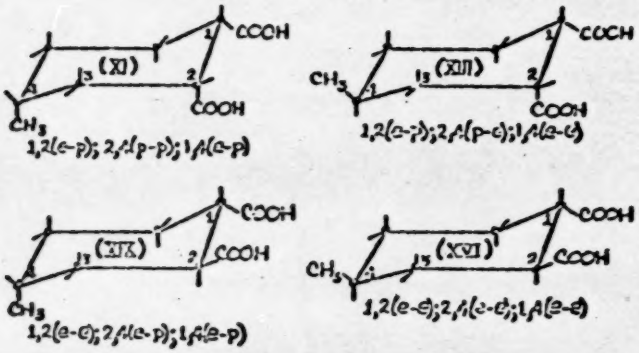
The formation of a single trans isomer, probably corresponding to the more stable configuration, prompted us to make a detailed study of the hydrogenation of the unsaturated trans acid (VII) and its anhydride (IX). As was to be expected, in neither of these cases was the hydrogenation selective.

It was found that in the hydrogenation of the trans anhydride (IX) in benzene solution over platinum oxide, a crystalline mixture of unsaturated trans anhydrides was formed. By treatment of this mixture with ether we succeeded in isolating a pure trans anhydride (XVIII), m.p. 121-122° in an amount equal to about one-third of the mixture taken. This trans anhydride differed from the trans anhydride (XVII) obtained from the trans acid (XVI), and it gave by hydrolysis the new trans acid (XIX), m.p. 164-165°. The crystalline mixture remaining after separation of the trans anhydride (XVIII) was crystallized from petroleum ether, and an apparently homogeneous crystalline product was obtained which melted over a range, 74-77°. Hydrolysis of this product with water yielded a mixture of acids, from which the trans acid (XVI) was isolated after three crystallizations from aqueous methanol. By crystallization from petroleum ether of a known mixture of the isomeric trans anhydrides (XVII) and (XVIII) it was shown that the crystalline product of m.p. 74-77° corresponded to a mixture of equal amounts of these trans anhydrides. Hence, in the hydrogenation of the trans anhydride (IX) a mixture of the isomeric saturated trans anhydrides (XVII) and (XVIII) is formed in the proportions of 1 : 2 approximately. The same ratio of isomers is obtained also in the hydrogenation of the trans acid (VII).



The isomeric trans dicarboxylic acids (XVI) and (XIX) were converted by reaction with diazomethane into the corresponding isomeric trans diesters (XX) and (XXI). It was found that, when boiled with sodium methoxide, the trans diester (XXI) was converted in good yield into the trans acid (XVI). The same transformation was readily effected also by heating the trans dicarboxylic acid (XIX) with concentrated hydrochloric acid. On the other hand, the isomeric trans anhydrides (XVII) and (XVIII), by simple heating at 210° for 30 minutes, were almost quantitatively isomerized into the same cis anhydride (XII), corresponding to trans-4-methyl-cis,cis-1,2-cyclohexanedicarboxylic acid (XIII).

When all of our results on the mutual transformations of the four isomeric 4-methyl-1,2-cyclohexane dicarboxylic acids are examined in the light of the theory of the "equatorial-polar" disposition of substituents, it is found that the geometric configurations of these acids can be established with exactness. The four isomeric 4-methyl-1,2-cyclohexanedicarboxylic acids can be represented by the following models:



For the two isomeric cis dicarboxylic acids (XI) and (XIII), the cis configuration of the 1- and 2-carboxyl groups (e-p) follows from the method of preparation (diene synthesis). On the assumption that the more equatorial arrangement of substituents will correspond to the more stable form, it follows that the more stable cis dicarboxylic acid (XIII) of m.p. 178° will have substituent configurations of 1,2-(e-p), 2,4-(p-e), and 1,4-(e-e) and will be trans-4-methyl-cis, cis-1,2-cyclohexanedicarboxylic acid. The isomeric cis acid (XI) will have the thermodynamically less advantageous substituent configurations of 1,2-(e-p), 2,4-(p-p), and 1,4-(e-p), and will be cis-4-methyl-cis, cis-1,2-cyclohexanedicarboxylic acid.

The diequatorial configuration of the trans-1,2 carboxyl groups in the trans acids (XVI) and (XIX) follows from the method of preparation (diene synthesis with fumaric ester) and from the readiness with which trans anhydrides are formed from them. Of the four isomeric acids, the trans dicarboxylic acid (XVI) is the most stable, and the other three acids (XI), (XIII), and (XIX) can be converted into it under various conditions (isomerization in presence of sodium methoxide or concentrated hydrochloric acid). This fact indicates that the trans acid (XVI) has the structure that is most advantageous energetically, and it should have the greatest number of equatorially disposed substituents. The trans dicarboxylic acid (XVI) should therefore be trans-4-methyl-cis, trans-1,2-cyclohexanedicarboxylic acid, having substituent configurations of 1,2-(e-e), 2,4-(e-e), and 1,4-(e-e). It follows that the isomeric trans acid (XIX) will be cis-4-methyl-cis, trans-1,2-cyclohexanedicarboxylic acid.

The numerous examples that are known of the thermal transformation of cyclic trans-1,2-dicarboxylic acids into the corresponding cis acids [9] find their explanation in the possibility of a transition under the influence of heat into a system having an energetically less advantageous arrangement of substituents (more polar). However, such a transformation, resulting in the formation of a cis isomer, should give the most stable of the possible cis configurations. This occurs, in fact, in the example that we have studied, for in the thermal isomerization reactions of the trans dicarboxylic acids (XVI) and (XIX) the same cis acid (XIII) is obtained, this having a geometric arrangement of substituents that is more advantageous energetically than the arrangement in the other possible cis configuration.

EXPERIMENTAL

Anhydride of trans-4-Methyl-cyclohexene-1,2-dicarboxylic Acid

A mixture of 2 g of the trans acid (VII) [10], m.p. 165-166°, and 20 ml of acetyl chloride was boiled until solution was complete (1.5-2 hours). The crystals remaining after removal of acetyl chloride by distillation were washed on the filter with a mixture of diethyl ether and petroleum ether (1 : 2). The product was 1.75 g of a substance of m.p. 141-143°. Two crystallizations from a mixture of benzene and petroleum ether (1 : 3) yielded the pure trans anhydride (IX), m.p. 146-147°.

	Found %:	C 65,11; 65,24; H 6,14; 6,15
$C_9H_{12}O_3$.	Calculated %:	C 65,04; H 6,06

When boiled with water, the trans anhydride (IX) gave a quantitative yield of the original trans acid (VII), m.p. 165-166°.

Thermal Isomerization of the trans Anhydride (IX)

The trans anhydride (IX) (1.2 g) was heated in an atmosphere of nitrogen at 200-210° for one hour. The light-brown melt solidified completely when cooled, and it had a melting point of 60-64°. Crystallization from a mixture of diethyl ether and petroleum ether yielded 0.8 g of a crystalline substance, m.p. 64-65°, undepressed by admixture of pure cis anhydride (IV) [7].

Hydrogenation of the cis-Anhydride (IV)

The cis anhydride (IV) [7] of m.p. 64-65° (7.0 g) was dissolved in 50 ml of absolute benzene and hydrogenated over platinum oxide. One molecular proportion of hydrogen (950 ml at 0° and 760 mm) was absorbed. The benzene was distilled off under reduced pressure, and the residue was dissolved in 20 ml of petroleum ether. The solution was left overnight under ice cooling. The crystals that separated were washed on the filter with a cold mixture of diethyl ether and petroleum ether (1 : 5), and 3.8 g of crystals melting at 33.5-35° was obtained. The solvents were distilled from the mother liquor, and the residue was dissolved in petroleum ether containing a little diethyl ether. The solution was cooled with solid carbon dioxide, and a further 0.7 g of crystals melting at 33-34.5° separated. The total yield of the saturated crystalline cis anhydride (X) was 4.5 g. After being crystallized from a mixture of diethyl ether and petroleum ether (1 : 2), the substance had a constant melting point of 35-36.5°.

	Found %:	C 64.19; 64.00;	H 7.32; 7.10
$C_9H_{12}O_3$.	Calculated %:	C 64.26;	H 7.20

The liquid residue remaining after separation of the cis anhydride (X) was hydrolyzed at the boil with 7 ml of water. The crystals obtained when the mixture cooled were washed on the filter with 10% aqueous methanol (1.9 g, m.p. 140-160°). Fractional crystallization from 50% methanol yielded 1.0 g of crystals melting at 174-177°. Recrystallization from 50% methanol yielded 0.85 g of the pure dicarboxylic acid (XIII), melting with decomposition at 177-178°. The trans-4-methyl-cis,cis-1,2-cyclohexanedicarboxylic acid described by Craig [8] melted at 177-178°.

cis-4-Methyl-cis,cis-1,2-cyclohexanedicarboxylic Acid (XI)

A mixture of 0.5 g of the cis anhydride (X), m.p. 35-36°, and 2 ml of water was boiled until solution was complete. When the solution was cool, 0.52 g of an acid, m.p. 171-175°, separated. Crystallization from water yielded the pure cis dicarboxylic acid (XI), m.p. 172-173°, identical with the acid described previously [8] and giving a depression of melting point in admixture with the cis dicarboxylic acid (XIII).

	Found %:	C 58.24; 58.15;	H 7.61; 7.63
$C_9H_{14}O_4$	Calculated %:	C 58.05;	H 7.59

When the cis dicarboxylic acid (XI) was boiled with acetyl chloride, a quantitative yield was obtained of the pure original anhydride (X), m.p. 34-36°.

Thermal Isomerization of the Anhydride of cis-4-Methyl-cis, cis-1,2-cyclohexanedicarboxylic Acid (X)

The cis anhydride (X) of m.p. 35-36° (3.8 g) was heated at 200-210° for 90 minutes in an atmosphere of nitrogen. Heating was continued for a further thirty minutes under reduced pressure at 240-250°, and the substance was then slowly distilled under reduced pressure at a bath temperature of 230-235°. The product was 2.4 g of a colorless viscous liquid (n_D^{20} 1.4795), and when this was boiled with water it yielded 2.2 g of a crystalline acid melting at 173-175°. Crystallization from 50% methanol yielded 1.8 g of pure trans-4-methyl-cis,cis-1,2-cyclohexanedicarboxylic acid (XIII), melting with decomposition at 177-178° and identical with the acid prepared previously.

Anhydride of trans-4-Methyl-cis,cis-1,2-cyclohexanedicarboxylic Acid (XII)

A mixture of 2.6 g of the dicarboxylic acid (XIII), m.p. 177-178°, and 25 ml of acetyl chloride was boiled until solution was complete (one hour). After removal of acetyl chloride under reduced pressure, the liquid reaction product, which did not crystallize when cooled and when treated with solvents, was vacuum-distilled. The product was 2.1 g of the cis anhydride (XII) in the form of a colorless viscous liquid, b.p. 127-128° (4 mm) and n_D^{20} 1.4790.

	Found %:	C 64.55; 64.39;	H 7.33; 7.33
$C_9H_{12}O_3$	Calculated %:	C 64.26;	H 7.20

When boiled with water, the cis anhydride (XII) gave a quantitative yield of the original cis dicarboxylic acid (XIII), which melted with decomposition at 176-178°.

Hydrogenation of cis-4-Methyl-4-cyclohexene-1,2-dicarboxylic Acid (VI)

The cis acid (VI) [7] of m.p. 154-155° (5.4 g) was dissolved in 50 ml of absolute methanol and hydrogenated over platinum oxide. When one molecular proportion of hydrogen (640 ml) had been absorbed the methanol was distilled off and 5.3 g of crystals melting at 160-166° was obtained. Recrystallization from 12 ml of 50% aqueous methanol yielded 3.8 g of the pure dicarboxylic acid (XI), melting at 172-173° and identical with the acid obtained previously. Evaporation of the mother liquor to dryness and two recrystallizations of the residue from 50% aqueous methanol yielded a further 0.8 g of the pure dicarboxylic acid (XI), m p. 172-173°. By fractional crystallization of the residues from aqueous methanol it was found possible to isolate about 50 mg of an acid melting at 176-177° and identical with the isomeric dicarboxylic acid (XIII) obtained previously.

Dimethyl Ester of cis-4-Methyl-cis,cis-1,2-cyclohexanedicarboxylic Acid (XIV)

A small excess of ethereal diazomethane was added to a suspension of 5 g of the dicarboxylic acid (XI), m.p. 171-173°, in 50 ml of ether. After removal of ether, the liquid reaction product was vacuum-distilled, and yielded 5.1 g of the cis diester (XIV), b.p. 110-110.5° (4 mm); n_D^{20} 1.4575; d_4^{20} 1.0782; found MR 54.11; calculated MR 54.17:

	Found %:	C 61.46; 61.51; H 8.31; 8.33
$C_{11}H_{18}O_4$	Calculated %:	C 61.66; H 8.47

Hydrolysis of the cis diester (XIV) with 20% aqueous caustic potash yielded the original cis dicarboxylic acid (XI), m.p. 171-173°.

Dimethyl Ester of trans-4-Methyl-cis,cis-1,2-cyclohexanedicarboxylic Acid (XV)

This was prepared by the procedure of the previous experiment from 3.6 g of the isomeric dicarboxylic acid (XIII), m.p. 176-178°. The distillation yielded 3.6 g of the cis diester (XV), b.p. 105-105.5° (3 mm); n_D^{20} 1.4572; d_4^{20} 1.0796; found M R 54.12; calculated MR 54.17:

	Found %:	C 61.62; 61.71; H 8.55, 8.55
$C_{11}H_{18}O_4$	Calculated %:	C 61.66; H 8.47

Hydrolysis of the cis diester (XV) with 20% caustic potash gave a good yield of the original cis dicarboxylic acid (XIII), m.p. 177-178°.

trans-4-Methyl-cis,trans-1,2-cyclohexanedicarboxylic Acid (XVI)

a) The cis diester (XIV) (2.1 g) was added to a solution of 4.7 g of sodium in 120 ml of absolute methanol, and the solution was boiled for 15 hours. The methanol was distilled off under reduced pressure, and the residue was dissolved in 40 ml of water. The solution was treated with charcoal and filtered, and was then evaporated in a porcelain dish on a water bath until a thick slurry was obtained. The precipitated salts were filtered off, washed on the filter with a little methanol, and dissolved in 10 ml of water. The solution was acidified with concentrated hydrochloric acid, and 1.5 g (83%) of a crystalline acid melting at 179-180° was obtained. Crystallization from 30% aqueous methanol yielded the pure trans dicarboxylic acid (XVI), which had a constant melting point of 181-182°.

	Found %:	C 58.05; 58.09; H 7.83, 7.66
$C_9H_{14}O_4$	Calculated %:	C 58.05; H 7.58

b) In a similar way, 2.8 g of the cis diester (XV) was boiled for 15 hours with a solution of 6.2 g of sodium in 160 ml of absolute methanol, and 1.8 g of a crystalline acid melting at 178-180° was isolated. After crystallization from 40% methanol it melted at 180-181°, and there was no depression in a mixture test with the trans dicarboxylic acid (XVI) obtained in the previous experiment. It gave a depression with the cis acid (XIII) (160-164°).

Anhydride of trans-4-Methyl-cis,trans-1,2-cyclohexanedicarboxylic Acid (XVII)

A mixture of 1.0 g of the trans dicarboxylic acid (XVI), m.p. 180-182°, and 20 ml of acetyl chloride was boiled until solution was complete (one hour). The excess of acetyl chloride was distilled off, and the liquid residue was heated in a vacuum at 80-85° for 20 minutes. Treatment with petroleum ether yielded a crystalline substance, which was washed on the filter with a cold mixture of diethyl ether and petroleum ether (1 : 5). The product was 0.65 g of a crystalline substance melting at 88-90°. After crystallization from a little ether, the trans anhydride (XVII) had a constant melting point of 96-97°.

	Found %:	C 64.29, 64.18; H 7.22, 7.25
$C_9H_{12}O_3$	Calculated %:	C 64.26; H 7.20

When the trans anhydride (XVII) was boiled with water, a quantitative yield of the original trans dicarboxylic acid (XVI), m.p. 180-181°, was obtained.

Hydrogenation of the Anhydride of trans-4-Methyl-4-cyclohexene-1,2-dicarboxylic Acid (IX)

The trans anhydride (IX) (5.5 g) was dissolved in 80 ml of cryoscopic benzene and hydrogenated over platinum oxide. The amount of hydrogen absorbed was 800 ml at 20° and 745 mm. The benzene was distilled off, and the liquid hydrogenation product that then remained gradually crystallized on standing. The crystalline substance was treated with a little warm benzene, and the undissolved part (0.3 g melting at 158-164°) was filtered off. The benzene was removed under reduced pressure, and the crystalline residue was washed on the filter with 50 ml of absolute ether. The product was 1.45 g of an ether-insoluble substance, m.p. 110-115°. Two recrystallizations of this from a small amount of a mixture of benzene and ether yielded the pure trans anhydride (XVIII) (1.2 g), which had a constant melting point of 121.5-122.5°.

	Found %:	C 64.49, 64.28; H 7.41, 7.24
$C_9H_{12}O_3$	Calculated %:	C 64.26; H 7.20

The ether solution remaining after separation of the trans anhydride (XVIII) was evaporated to dryness, and 3.55 g of a crystalline substance melting at 65-75° was obtained. This substance was heated with 200 ml of petroleum ether, and the undissolved residue was filtered off. A substance of m.p. 90-140° (0.4 g) was obtained, and from this, after washing on the filter with a little ether and crystallization from 40% aqueous methanol, 0.15 g of the trans dicarboxylic acid (XVI), m.p. 180-181°, was isolated.

The petroleum ether solution was evaporated to small bulk, and 2.15 g of a crystalline substance, m.p. 72-75°, was obtained. The product was readily soluble in ether, and it crystallized from petroleum ether in the form of apparently homogeneous needles having a melting range of 73-77°. Attempts to isolate individual substances by crystallization were unsuccessful, and 1.2 g of this crystalline mixture was hydrolyzed at the boil with 5 ml of water. The resulting crystalline mixture of acids (m.p. 168-175°) was crystallized three times from 40% methanol, and 0.5 g of the trans dicarboxylic acid (XVI) was obtained. It melted at 179-181°, and gave no depression in admixture with an authentic sample.

A mixture of equal amounts of the pure trans anhydrides (XVII) and (XVIII) was crystallized from petroleum ether and then melted at 74-77°; there was no depression in a mixture test with the mixture of anhydrides obtained in the experiment described above.

Hydrogenation of trans-4-Methyl-4-cyclohexene-1,2-dicarboxylic Acid (VII)

The trans acid (VII) (4.2 g) was dissolved in 40 ml of methanol and hydrogenated over platinum oxide. One molecular proportion of hydrogen (515 ml) was absorbed. The thick liquid remaining after removal of methanol rapidly solidified when a little water was added. The product was 4.1 g of a mixture of acids melting at 160-165°, and it was not found possible to separate the acids by crystallization. The acids were converted into their anhydrides by boiling the mixture with 40 ml of acetyl chloride for two hours. The residue remaining after removal of acetyl chloride was treated with petroleum ether, and 2.85 g of a crystalline mixture of anhydrides melting at 73-90° was obtained. Treatment of the mixture with ether yielded 0.8 g of the pure trans anhydride (XVIII), m.p. 121-122°, and 1.6 g of an unresolvable mixture of the trans anhydrides (XVII) and (XVIII), m.p. 74-76°, which was hydrolyzed to a mixture of acids. Three crystallizations of the mixture of acids from 40% methanol yielded 0.6 g of the pure trans dicarboxylic acid (XVI), m.p. 180-181°.

cis-4-Methyl-cis,trans-1,2-cyclohexanedicarboxylic Acid (XIX)

A mixture of 0.6 g of the trans anhydride (XVIII), m.p. 121-122°, and 2.5 ml of water was boiled until solution was complete (five minutes). On cooling, the solution yielded 0.05 g of crystals of the trans dicarboxylic acid (XIX), m.p. 161-162°. After being crystallized from 20% aqueous methanol they had a constant melting point of 162-164°.

	Found %:	C 57.82; 57.83; H 7.45; 7.59
$C_9H_{14}O_4$	Calculated %:	C 58.05; H 7.58

When treated with excess of acetyl chloride, the dicarboxylic acid (XIX) was converted in good yield into the original trans anhydride (XVIII), m.p. 120-121°.

Dimethyl Ester of trans-4-Methyl-cis,trans-1,2-cyclohexanedicarboxylic Acid (XX)

Treatment of 3 g of the trans dicarboxylic acid (XVI), m.p. 181-182°, with excess of ethereal diazomethane,

followed by vacuum distillation, gave 3.1 g of the trans diester (XX), b.p. 110-110.5° (4 mm); n_D^{20} 1.4535; d_4^{20} 1.0660; found MR 54.38; calculated MR 54.11.

	Found %:	C 61.59, 61.55; H 8.65, 8.55
$C_{11}H_{18}O_4$.	Calculated %:	C 61.66; H 8.47

Hydrolysis of the trans diester (XX) with 20% caustic potash gave a good yield of the original trans dicarboxylic acid (XVI), m.p. 180-181°.

Dimethyl Ester of cis-4-Methyl-cis,trans-1,2-cyclohexanedicarboxylic Acid (XXI)

By the procedure of the previous experiment 1.0 g of the trans dicarboxylic acid (XIX), m.p. 163-164°, yielded 1.05 g of the trans diester (XXI), b.p. 111° (5 mm); n_D^{20} 1.4570; d_4^{20} 1.0800; found MR 54.03; calculated MR 54.11.

	Found %:	C61.38, 61.45; H 8.52, 8.64
$C_{11}H_{18}O_4$.	Calculated %:	C 61.66; H 8.47

Hydrolysis of the trans diester (XXI) with 20% caustic potash gave the original trans acid (XIX), m.p. 162-164°.

Isomerization of the trans Dicarboxylic Acid (XIX) and its Diester (XXI)

a) A mixture of 0.5 g of the trans dicarboxylic acid (XIX), m.p. 163-164°, and 5 ml of concentrated hydrochloric acid was heated in a sealed glass tube at 170-175° for seven hours. Hydrochloric acid was distilled off, and crystallization of the residue from 40% aqueous methanol yielded 0.3 g of acid melting at 181-182°, identical with the trans acid (XVI).

b) The trans diester (XXI) (0.4 g) was added to a solution of 1 g of sodium in 30 ml of absolute methanol, and the mixture was boiled for 15 hours. The methanol was distilled off, and the residue was dissolved in 10 ml of water. The solution was evaporated down to a thick slurry in a porcelain dish. The precipitate of salts was filtered off, washed with methanol, and dissolved in 2 ml of water. Acidification of the solution with concentrated hydrochloric acid yielded 0.3 g of the trans acid (XVI), m.p. 180-181°, undepressed by admixture of a known sample.

Thermal Isomerization of the trans Anhydrides (XVII) and (XVIII)

a) The trans anhydride (XVII) of m.p. 96-97° (0.5 g) was heated in nitrogen at low pressure for one hour at 210-215°. The reaction product was vacuum-distilled at a bath temperature of 200-205° (n_D^{20} 1.4795) and then hydrolyzed at the boil with 2 ml of water. The product was 0.4 g of a crystalline acid melting at 173-175°. After being crystallized from 50% aqueous methanol, it melted at 177-178°, and there was no depression in a mixture test with a pure sample of the cis dicarboxylic acid (XIII).

b) Similarly, 0.5 g of the trans anhydride (XVIII), m.p. 121-122°, after being heated and vacuum-distilled, yielded a liquid having n_D^{20} 1.4790. Hydrolysis gave 0.4 g of an acid melting at 175-176°. Crystallization from 50% methanol gave the pure cis dicarboxylic acid (XIII), m.p. 177-178°, undepressed by an authentic sample.

SUMMARY

1. All four theoretically possible isomers of 4-methyl-1,2-cyclohexanedicarboxylic acid have been prepared by the hydrogenation of cis- and trans-4-methyl-4-cyclohexene-1,2-dicarboxylic acids (VI) and (VII) and of their anhydrides (IV) and (IX).

2. A study has been made of the mutual stereochemical conversions of these four isomers under the influence of heat and of isomerization agents, and this has enabled us to determine the relative stabilities of the individual forms of the cis and trans series.

3. The geometric configurations of all four isomeric 4-methyl-1,2-cyclohexanedicarboxylic acids have been examined on the basis of the theory of the "equatorial-polar" arrangement of substituents.

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CATALYTIC AMINATION OF ALCOHOLS

M.A. Popov and N.I. Shuikin

The catalytic amination of alcohols has been the subject of numerous investigations. The investigators have usually confined themselves to a search for efficient catalysts and the determination of optimum conditions for preparing amines. Only occasionally have they attempted to determine what intermediate compounds are formed in the conversion of the alcohol into an amine. The solution of this problem, however, would be valuable, not only for the theory of catalysis, but also as an aid to the selection of the catalyst and reaction conditions in the synthesis of amines.

Sabatier and Maihle [1], on the basis of experiments on the amination of alcohols in presence of thorium oxide, considered that unstable alkyl thorates were first formed, and these then reacted with ammonia, giving primary amines. The latter, in their turn, also reacted with alkyl thorates giving secondary amines, and in a similar way the secondary amines were converted into tertiary amines. According to Sabatier, therefore, amination proceeds in two stages: first the alcohol reacts with the metal oxide, and then the esterlike compound formed reacts with ammonia with elimination of water and formation of an amine. For this reason these authors used various metal oxides as catalysts for the amination of alcohols.

Similar ideas have been expressed by other investigators, who have used metal oxides as catalysts for the amination of alcohols and consider that the formation of an intermediate compound between the alcohol and the catalyst must occur [2]. Shuikin, Balandin, and Pletkin, in a paper on the amination of ethanol [3], have expressed a different view, namely, that the conversion of the alcohol into the amine occurs by the redistribution of bonds on the surface of the active centers of the catalyst, without formation of intermediate compounds.

Schwegler and Adkins [4], who made use of Mignonac's ideas concerning the reactions of aldehydes and ketones with ammonia, considered that aldehydes or ketones are formed intermediately in the amination of alcohols, and these then react with ammonia. The resulting imines are reduced by hydrogen, giving primary amines. Similarly, reaction of the primary amines with carbonyl compounds yields secondary amines, and from the secondary amines tertiary amines are formed. Since the rates of these reactions vary, carbonyl compounds are found in the condensate. According to this scheme, tertiary alcohols, being unable to yield either aldehydes or ketones, cannot give amines. Ipatin [5] considers that in the amination of alcohols ethers are first formed, and these then react with ammonia with formation of primary and secondary amines. On this scheme the formation of tertiary amines will be improbable, and its author suggests, therefore, that tertiary amines arise " in the usual way" from secondary amines and alcohols.

We set ourselves the task of determining experimentally whether or not these reaction schemes for the conversion of alcohols into amines were in accord with the actual course of the reactions. We have investigated the catalytic amination of alcohols, aldehydes, ketones, and ethers, the substances used being ethanol, 2-propanol, 1- and 2-butanols, cyclohexanol, acetaldehyde, butyraldehyde, acetone, 2-butanone, cyclohexanone, diethyl ether, butyl ethyl ether, and diisopentyl ether. The results for the amination of 1- and 2-butanols and of the ketones are taken from our previous papers [6]. Platinized silica gel and activated wood charcoal were used as catalysts; these have been shown to have high amination activity [7].

EXPERIMENTAL

The properties of the alcohols, aldehydes, and ethers used in the investigation are given in Table 1.

In the experiments, the vapor of the organic compound together with ammonia— and for the amination of aldehydes and ketones, also an excess of hydrogen —was passed into the catalysis tube, which was situated in an electric furnace. In each experiment the amount of catalyst taken was 100 ml; the preparation of the catalysts has been described previously [7]. The duration of each experiment was one hour.

The liquid part of the catalyzate was dried, and the contents of primary, secondary, and tertiary amines were determined by Weber and Wilson's method, ammonia being first removed by Francois' method. However, the use of only the analytical method for the investigation of the complex condensates obtained in the amination of alcohols and carbonyl compounds is inadequate, for at high reaction temperatures other basic substances may be formed. In some experiments, therefore, the isolation and investigation of the amines was carried out. The amines isolated were converted into chloroplatinates, which were analyzed for platinum.

TABLE 1

Properties of Starting Materials

Substance	B.p. (°C)	Pressure (mm Hg)	d_4^{20}	n_D^{20}	Literature references
Ethanol	78	758	0.8792	1.3611	[8, 9, 10]
2-Propanol	82	756	0.7855	1.3772	[8, 11]
Acetaldehyde	21	758	0.7836	1.3320	[12]
Butyraldehyde	74	752	0.8166	1.3842	[13]
Diethyl ether	35	752	0.7134	1.3540	[14]
Butyl ethyl ether	92	752	0.7457	1.3770	[15]
Diisopentyl ether	171	754	0.7724	–	[16, 17]

Information on the experimental conditions and the contents of amines in the condensates is given in Tables 2 and 3.

Elementary-analysis results for amines isolated from the amination condensates of ethanol, the butanols, and the ketones are given in Table 4. The boiling points of the amines obtained and the platinum contents of their chloroplatinates are given in Table 5.

In the reductive amination of acetaldehyde over platinized silica gel and over active charcoal, solid condensates were obtained, and investigation showed them to be aldehyde-ammonia. The amines were extracted with hydrochloric acid from 49 g of the condensate obtained in the reductive amination of butyraldehyde over platinized silica gel. They were then liberated with caustic alkali, dried, and fractionally distilled, when the following fractions were obtained:

Fraction I B.p. 75-77° (754 mm); 2.7 g
Fraction II B.p. 157-162° (754 mm); 2.8 g
Fraction III B.p. 210-220° (754 mm); 0.5 g

TABLE 2

Experimental Conditions for the Catalytic Amination of Alcohols, Carbonyl Compounds, and Ethers

Original substance	Platinum catalyst					Active charcoal catalyst				
	Temperature of experiment (°C)	Amount taken (g)		Amount of condensate (g)	Nitrogen content of amines (%)	Temperature of experiment (°C)	Amount taken (g)		Amount of condensate (g)	Nitrogen content of amines (%)
		Organic substance	Ammonia				Organic substance	Ammonia		
Ethanol	400	10.5	14.5	11.0	2.1	450	12.5	12.3	11.0	5.3
2-Propanl	300	15.7	10.8	17.5	1.4	450	15.7	10.8	13.0	7.7
1-Butanol	450	18.1	20.5	6.6	5.9	350	20.7	11.0	8.0	3.3
2-Butanol	300	16.8	13.4	12.0	1.4	350	16.0	14.8	11.0	3.6
Cyclohexanol	320	9.0	4.9	6.0	3.8	320	9.7	4.9	7.3	3.3
Acetaldehyde	Does not give amines					Does not give amines				
Butyraldehyde	400	8.1	4.0	7.7	2.4	350	8.2	4.1	8.6	8.3
Acetone	300	6.0	2.6	5.2	6.5	450	8.0	4.1	6.5	6.4
2-Butanone	290	6.4	4.5	6.7	2.9	350	8.1	5.0	5.2	2.4
Cyclohexanone	320	9.0	5.1	8.0	2.2	350	9.0	4.5	9.1	3.2
Diethyl ether	400	16.4	12.4	10.0	0.45	450	14.9	10.7	8.0	0.9
Butyl ethyl ether	450	11.9	7.3	9.2	1.03	–	–	–	–	–
Diisopentyl ether	450	16.1	5.9	9.9	1.03	450	19.1	8.3	16.6	1.02

The elementary analyses of these fractions were (%):

Fraction I: C 65.62; H 15.23; N 19.10
Fraction II: C 74.13; H 15.12; N 11.08
Fraction III: C 77.78; H 14.80; N 7.48

The results indicated that Fraction I was mainly butylamine, Fraction II mainly dibutylamine, and Fraction III mainly tributylamine.

TABLE 3

Amine Contents in Condensates from the Amination of Alcohols and the Corresponding Carbonyl Compounds

Original Substance	Platinum catalyst				Active charcoal catalyst			
	Amine content of condensate (%)				Amine content of condensate (%)			
	Primary	Secondary	Tertiary	Total	Primary	Secondary	Tertiary	Total
Ethanol	5.9	1.6	0.9	8.4	10.6	6.5	5.0	22.1
2-Propanol	0.8	3.6	7.2	11.6	7.2	26.4	24.0	57.6
1-Butanol	5.5	4.6	57.7	67.8	3.4	20.1	6.3	29.8
2-Butanol	7.3	–	–	7.3	13.3	–	14.2	27.5
Cyclohexanol	26.4	–	–	26.4	22.4	–	–	22.4
Acetaldehyde	Does not give amines				Does not give amines			
Butyraldehyde	5.4	5.6	1.0	12.0	–	–	6.2	6.2
Acetone	27.5	–	–	27.5	26.9	–	–	26.9
2-Butanone	15.1	–	–	15.1	12.5	–	–	12.5
Cyclohexanone	15.4	–	–	15.4	22.4	–	–	22.4

TABLE 4

Results of the Elementary Analysis of the Amines Isolated

Amine	Found %			Calculated %		
	C	H	N	C	H	N
Ethylamine	53.13	15.64	31.10	53.25	15.65	31.08
Diethylamine	65.61	15.20	19.12	65.66	15.17	19.15
Triethylamine	71.25	15.02	13.79	71.20	14.95	13.84
Butylamine	65.59	15.43	19.10	65.66	15.17	19.15
Dibutylamine	74.17	14.95	11.09	74.32	14.82	10.83
Tributylamine	77.75	14.71	7.62	77.74	14.69	7.55
Isopropylamine	60.83	15.40	23.47	60.94	15.35	23.71
sec-Butylamine	65.56	15.19	19.09	65.66	15.17	19.15
Cyclohexylamine	72.52	13.28	14.14	72.65	13.22	14.12

TABLE 5

Boiling Points of the Amines Isolated and Analytical Data for their Chloroplatinates

Amine	Boiling point of amine			Platinum content of chloroplatinate (%)	
	Found	Reported in literature	Literature		
	in °C (p in mm Hg)	in °C (p in mm Hg)	reference	found	calculated
Diethylamine	55-56 (756)	55-56 (767.8)	[20]	35.01	35.09
Triethylamine	88-89 (756)	89-89.5 (736.5)	[21]	31.79	31.88
Butylamine	76-77 (756)	77.8 (760.4)	[22]	35.11	35.09
Dibutylamine	159 (756)	159 (761)	[22]	29.25	29.21
Tributylamine	215-216 (753)	216.5	[22]	25.10	25.01
Isopropylamine	33-35 (748)	33-34	[23]	36.81	36.96
sec-Butylamine	61-63 (750)	63 (750)	[24]	34.97	35.09
Cyclohexylamine	133-135 (755)	133-134	[25]	32.11	32.09

From 24 g of the condensate from the reductive amination of butyraldehyde over active charcoal the following fractions were isolated by the method indicated above:

Fraction I B. p. 85-214° (752 mm): 0.2 g
Fraction II B. p. 214-219° (752 mm): 1.5 g
Residue 11.5 g

The elementary analysis of Fraction II was (%): C 77.80; H 14.61; N 7.78.

On the basis of these results Fraction II corresponds to tributylamine.

The results on the catalytic synthesis of amines obtained from the amination condensates of cyclohexanol [26] and of the ketones used in these experiments [6] have been described previously. It was established that in the catalytic amination of aliphatic alcohols, not only amines, but also nitriles, aldehydes, ketones, saturated and unsaturated hydrocarbons, hydrogen, and water were formed.

The catalyzates obtained by the amination of ethers were not investigated in detail on account of their low amine contents.

DISCUSSION OF RESULTS

The experiments on the amination of alcohols have established that amines are formed in considerable amounts in presence of platinized silica gel or active charcoal.

It is impossible to imagine, however, that alcohols could form intermediate compounds with these catalysts. It must be considered that Sabatier and Maihle's ideas relating to the formation of an intermediate compound between the alcohol and the catalyst in the course of the amination do not apply in these cases.

Baum's proposed reaction scheme for the amination of alcohols is also not supported by our investigations. The experiments showed that ethers gave much lower yields of amines than alcohols did. This is true for catalysts other than these used by us; in his dissertation Baum gives tables in which it is shown that in presence of alumina, butyl alcohol treated with ammonia at 450° at a molar ratio of ammonia to alcohol of three gives 39.5% of amines. On the other hand, dibutyl ether, at the same ratio of ammonia to ether, yields 32.8% of amines at 300°, and is decomposed completely at 450° with formation of an olefin and water. A further defect of this scheme is that it is in conflict with the fact that tertiary amines are formed. Here Baum is forced to abandon his scheme and refer to some "urual way" in which the tertiary amines are considered to be formed.

With regard to Mignonac's scheme for the explanation of the formation of amines from alcohols via the intermediate stage of carbonyl compounds, in order to resolve the question of its validity it is sufficient to compare our amination results for alcohols with those for the corresponding aldehydes and ketones. The experiments have shown that there is a considerable difference, both in the total yield of amines, and also in the relative amounts of primary, secondary, and tertiary amines. It may be pointed out here that primary alcohols give much higher yields of amines than the corresponding aldehydes do, irrespective of the catalyst used. This is a result of the far-reaching changes and resinification undergone by aldehydes and aldehyde-ammonias under the conditions of the experiments. It is only in the presence of active charcoal that secondary alcohols are aminated more readily than the corresponding ketones; on platinized silica gel these alcohols give lower yields of amines than the ketones do. Only in one case, the amination of cyclohexanol and cyclohexanone over active charcoal, were identical yields of amine (cyclohexylamine) obtained. Hence, with rare exceptions, it is impossible to regard aldehydes and ketones as intermediates in the amination of alcohols.

The results of our experiments give us reason to maintain that the process of the amination of alcohols consists in the simple elimination of the elements of water from the alcohol and ammonia at the catayst surface without the formation of intermediate compounds. By the same dehydration process the primary amine yields a secondary amine, and the secondary a tertiary. However, the rates of these dehydration reactions occuring simultaneously between the alcohol and ammonia, primary amine, and secondary amine are different. The relative amounts of the various amines formed will therefore be different.

Also, the dehydration reaction may be confined to the alcohol molecule, so that unsaturated hydrocarbons will be formed. It is known that water is particularly readily eliminated from tertiary alcohols, and these therefore form mainly unsaturated hydrocarbons, and not amines. Aldehydes and ketones arise under amination conditions as a result of the dehydrogenation of alcohols. When these carbonyl compounds react with ammonia and hydrogen, amines may again be formed, though in insignificant amount. In particular cases, in the amination of certain secondary alcohols, there is no reason to reject this method of amine formation. It occurs when the ketone formed can undergo amination at temperatures of the order of 350° and higher.

SUMMARY

1. The view that alcohols are converted into amines with intermediate formation of aldehydes, ketones, ethers, or unstable compounds between the alcohol and the catalyst is not supported by experiment.

2. In the catalytic amination of alcohols, amines are formed by the direct elimination of the elements of water from molecules of alcohol and ammonia or alcohol and amine, when these come together at the catalyst surface.

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REACTIONS OF INDIVIDUAL HYDROCARBONS IN CONTACT WITH NATURAL ALUMINOSILICATES

COMMUNICATION 3. REACTIONS OF CYCLOPENTANE, ETHYLCYCLOPENTANE, ETHYLCYCLOHEXANE, AND ETHYLBENZENE IN PRESENCE OF TROSHKOV CLAY

N. I. Shuikin and E. A. Timofeeva

In our preceding communication [1] we have given the results of an investigation of the behavior of cyclohexane, methylcyclohexane, and toluene in contact with Troshkov clay. The behavior of the two cycloalkanes indicates that the higher the molecular weight of the cycloalkane, the greater the extent of its conversion into other products. This work shows also that, under the conditions of the catalysis, alkylation, which proceeds simultaneously with dehydrogenation of the cycloalkanes, is the predominant reaction.

The present paper describes a study of the reactions of two five-membered cycloalkanes – cyclopentane and ethylcyclopentane – and also of ethylcyclohexane and ethylbenzene. In the main, the results confirm the regularities observed in the previous investigation.

EXPERIMENTAL

Cyclopentane was prepared by depolymerization of the dimer of cyclopentadiene in a continuous apparatus [2], followed by hydrogenation of the resulting cyclopentadiene in presence of finely dispersed nickel carried by aluminum. Ethylcyclopentane was synthesized from adipic acid via cyclopentanone, 1-ethylcyclopentanol, and 1-ethylcyclopentene. Ethylcyclohexane was prepared by the catalytic hydrogenation of ethylbenzene in presence of a nickel catalyst and hydrogen under pressure. The hydrocarbons prepared in this way were distilled through a 70-plate column. They had the following properties:

	B.p. in °C (corr.)	n_D^{20}	d_4^{20}
Cyclopentane	48.5–49.5	1.4070	0.7462
Ethylcyclopentane	103.2–103.4	1.4190	0.7664
Ethylcyclohexane	131.0	1.4335	0.7878
Ethylbenzene	136.0	1.4960	0.8670

All experiments were carried out in the usual continuous-flow apparatus at 500° and atmospheric pressure, and the same portion of catalyst was used throughout (volume 100 ml, weight 93.1 g, length of layer 43.5 cm, internal diameter of catalysis tube 20 mm). The Troshkov (Siberian) clay was activated with sulfuric acid. Its chemical composition is given in one of our papers [3]. When the experiments on a given hydrocarbon had been completed, the catalyst was regenerated by oxidation with air at 500° for 4–5 hours.

Reactions of Cyclopentane

Cyclopentane was passed in 25 ml (18.6 g) portions at a space velocity of 0.15. The results of the experiments are summarized in Table 1.

The results obtained when the united catalyzate from all experiments (41.8 g) was distilled through a 70-plate column are given in Table 2.

Fraction I was treated with 82% sulfuric acid in order to remove unsaturated hydrocarbons. After being washed with water and dried over calcium chloride, this fraction came over in the range 34.2–49.0° (752 mm) when distilled over sodium, and it had n_D^{20} 1.3960; d_4^{20} 0.7325, and aniline point 21.2° (in a sealed tube). The high aniline point (the aniline point of cyclopentane is 18°) indicates that this fraction contained not only unchanged cyclopentane and C_5 unsaturated hydrocarbons, but also n-pentane. Fraction II was practically

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naphthene-paraffin part was completely free of aromatics (negative formolite test) and unsaturated hydrocarbons (Bayer test). The fractionation curves for the two parts of the catalyzate are shown in Figures 1 and 2.

TABLE 3

Properties of Ethylcyclopentane Catalyzates

Expt. no.	Yield of catalyzate (%)	Yield of gas (liter, NTP)	Properties of Catalyzate				
			n_D^{20}	d_4^{20}	Content of sulfonatable hydrocarbons (% by volume)	Iodine number	Content of unsaturated hydrocarbons (% by weight)
1	96.1	4,153	1.4280	–	22.0	–	–
2	95.0	4,631	1.4310	–	–	–	–
3	93.0	5,325	1.4280	0.7730	22.0	11.6	4.6
4	93.0	5,133	1.4320	–	–	–	–
5	94.0	5,286	1.4320	0.7746	25.0	12.0	4.7
6	92.0	5,066	1.4310	–	–	–	–
7	96.1	4,914	1.4296	0.7752	23.0	10.6	4.1
8	93.0	5,996	1.4325	–	–	–	–

TABLE 4

Properties of Fractions of the United Ethylcyclopentane Catalyzate

Fraction no.	Boiling range (°C corr.)	Amount (g)	n_D^{20}	d_4^{20}	Iodine number	Aniline point
		From the naphthene-paraffin part				
I	68.2 – 92.6	3.6	1.4035	0.7281	–	50.5
II	92.6–102.9	8.5	1.4160	0.7618	–	40.5
III	102.9–103.3	134.0	1.4136	0.7640	–	–
Residue		0.3	1.4200	–	–	–
		From the aromatic part (together with unsaturated hydrocarbons)				
IV	57.9 – 78.9	1.1	1.4130	0.7198	266.5	–
V	78.9–102.3	1.9	1.4300	0.7466	184.9	–
VI	102.3–115.0	22.9	1.4860	0.8523	23.7	–
VII	115.0–200.0	13.2	1.5240	0.9062	0.9	–
Residue		0.4	1.5280	–	–	–

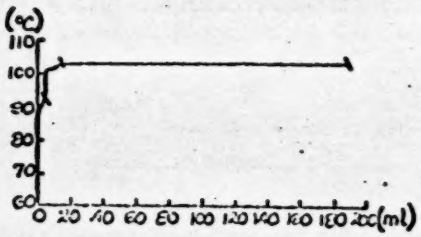


Fig. 1. Fractionation curve of the naphthene-paraffin part of the ethylcyclopentene catalyzate.

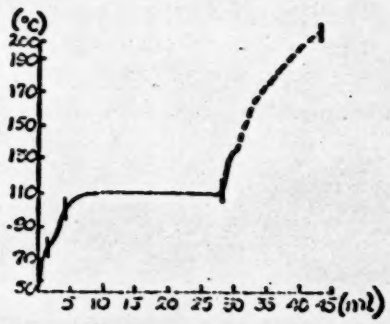


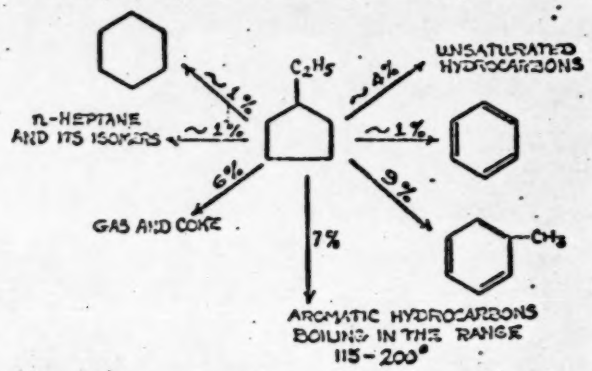
Fig. 2. Fractionation curve of aromatic part (together with unsaturated hydrocarbons) of the ethylcyclopentane catalyzate

Fraction I of the naphthene-paraffin part of the catalyzate was submitted to exhaustive dehydrogenational catalysis. Its refractive index was then raised from 1.4035 to 1.4310. After removal of the benzene formed, the fraction had n_D^{20} 1.3850, d_4^{20} 0.6798, and an aniline point of 70°. Fraction I, therefore, contained cyclohexane and, judging from the properties of the dearomatized catalyzate, also heptane isomers. The rather high aniline point (40.5°) of Fraction II (92.6–102.9°), as compared with the aniline point of pure ethylcyclopentane (38.7°), indicates that it contained some heptane isomers. Fraction III (102.9–103.3°) was almost pure unchanged ethylcyclopentane.

Fraction IV of the aromatic part of the catalyzate had an iodine number of 260.5 and consisted mainly of unsaturated hydrocarbons; it is possible, however, that this small fraction contained a little benzene. Fraction V, judging by its properties, boiling range, and high iodine number, contained an appreciable amount of C_7 unsaturated hydrocarbons, and the value of the iodine number indicates that the content of unsaturated hydrocarbons was about 70%, the remainder being apparently benzene. The properties of Fraction VI show (see also the fractionation curve) that it was mainly toluene, but the iodine number indicates that it contained also about 10% of C_8 unsaturated hydrocarbons. Fraction VIII contained a little toluene, but consisted mainly of xylenes and higher benzene homologs (see fractionation curve).

Hence, as a result of the passage of ethylcyclopentane in contact with activated Troshkov clay under the given conditions, 22% of sulfonatables was obtained, and this consisted mainly of aromatic hydrocarbons, since the iodine number of the united catalyzate was only 11.4. These consisted mainly of toluene (9%), formed, no doubt, as a result of the isomerization of ethylcyclopentane to methylcyclohexane and the dehydrogenation of the latter. The yield of benzene and its higher homologs amounted to about 7%, calculated on the original hydrocarbon. In addition, cleavage of the five-membered ring occurred, with formation of about 1% of n-heptane and its isomers.

The observed reactions of ethylcyclopentane can be represented by the following scheme:



The degree of conversion was 26-28%.

Reactions of Ethylcyclohexane

Ethylcyclohexane was passed over the same catalyst, after regeneration, in 50 ml (39.4 g) portions at a space velocity of 0.3. Altogether, 450 ml (354.5 g) of hydrocarbon was passed. The properties of the resulting catalyzates are given in Table 5.

The united catalyzate from all experiments had n_D^{20} 1.4450; d_4^{20} 0.7912; and iodine number 0.9, and it contained 30.0% by volume of sulfonatable hydrocarbons.

Analysis of gas

	Expt. No. 3	Expt. No. 8
Unsaturated hydrocarbons	12.3%	12.8%
Hydrogen	58.1%	54.1%
Paraffin hydrocarbons	29.6%	33.1%

The catalyzate (312.5 g) was separated into naphthene-paraffin and aromatic parts by adsorption on silica gel. The naphthene-paraffin part of the catalyzate was quite free from unsaturated and aromatic hydrocarbons (negative Bayer and formolite tests). The fractionation curves for the two parts of the catalyzate are given in Figures 3 and 4.

The properties of the fractions so obtained are given in Table 6. The naphthene-paraffin part of the catalyzate was fractionated through a 70-plate column, and the aromatic part—through a 20-plate column.

TABLE 5

Properties of Ethylcyclohexane Catalyzates

Expt. no.	Yield of catalyzate (%)	Yield of gas (liter, NTP)	Properties of catalyzate			
			n_D^{20}	d_4^{20}	Content of sulfonatable hydrocarbons (% by volume)	Iodine number
1	80.5	6.758	1.4430	0.7906	30.0	0.7
2	84.9	7.280	1.4430	–	–	–
3	85.3	7.528	1.4460	0.7951	30.0	1.0
4	86.0	7.282	1.4425	–	–	–
5	86.0	7.368	1.4420	0.7908	27.0	0.9
6	85.9	7.565	1.4460	–	–	–
7	85.3	7.397	1.4450	0.7909	–	0.9
8	86.0	7.960	1.4450	–	–	–
9	86.0	7.538	1.4460	–	32.0	–

TABLE 6

Properties of Fractions of the Ethylcyclohexane Catalyzate

Fraction no.	Boiling range (°C corr.)	Amount (g)	n_D^{20}	d_4^{20}	Iodine number	Aniline point
			From the naphthene-paraffin part			
I	47.8 – 81.8	4.2	1.3910	0.7018	–	70.8
II	81.8 – 130.1	25.3	1.4260	0.7755	–	46.8
III	130.1 – 131.0	125.0	1.4325	0.7865	–	44.0
Residue		0.4	1.4395	–	–	–
			From the aromatic part			
IV	58.8 – 78.3	1.7	1.4245	0.7731	52.1	–
V	78.3 – 83.1	2.3	1.4560	–	54.0	–
VI	83.1 – 122.5	15.7	1.4910	0.8568	4.2	–
VII	122.5 – 140.0	21.5	1.4900	0.8596	0.0	–
VIII	140.0 – 147.0	32.5	1.4920	0.8660	7.3	–
IX	147.0 – 210.0	11.4	1.5061	0.8787	11.5	–
Residue		0.5	1.5130	–	–	–

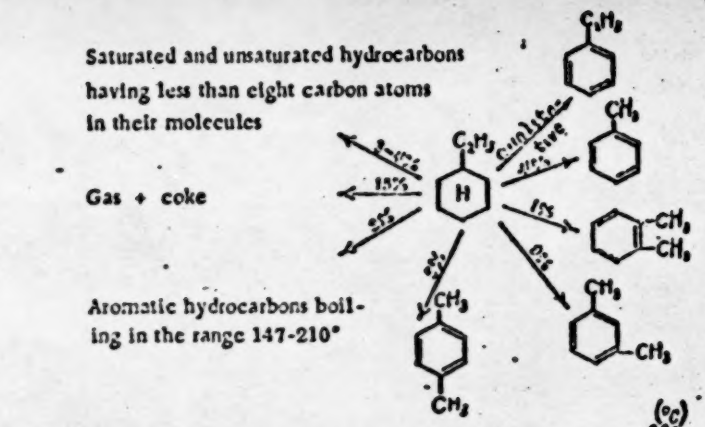
Fraction I, judging from its properties, consisted of alkanes. Investigation of Fractions II and III by the Raman-spectrum method indicated that they consisted mainly of unchanged ethylcyclohexane. The properties of Fraction II, however, indicated that it contained also a small amount of alkanes.

The compositions of the fractions obtained from the aromatic part of the catalyzate were determined by the Raman-spectrum method. It was found that Fractions IV and V consisted of a mixture of unsaturated hydrocarbons and benzene. Fraction VI contained a considerable amount of toluene and traces of unsaturated hydrocarbons. Fractions VII and VIII consisted of m-xylene (about 60%), p-xylene (about 27%), o-xylene (about 6%), and a little ethylbenzene. Fraction IX contained higher benzene homologs boiling over the range 147-210°, in admixture with unsaturated hydrocarbons.

Hence, the main reactions of ethylcyclohexane in contact with activated Trokhkov clay consisted in the formation of aromatic hydrocarbons, namely, toluene, isomeric xylenes, ethylbenzene, and higher benzene homologs boiling in the range 147-210°; at the same time a small amount of alkanes was formed.

The contact-catalysis reactions of ethylcyclohexane under the given conditions may be represented schematically as follows: (see top of following page).

The degree of conversion was 40-41%.


Saturated and unsaturated hydrocarbons having less than eight carbon atoms in their molecules
Gas + coke
Aromatic hydrocarbons boiling in the range 147-210°
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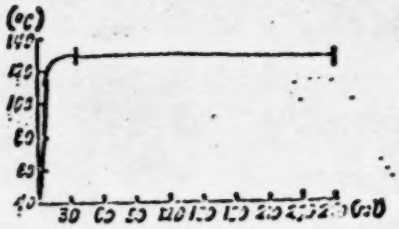

Fig. 3. Fractionation curve of the naphthene-paraffin part of the ethylcyclohexane

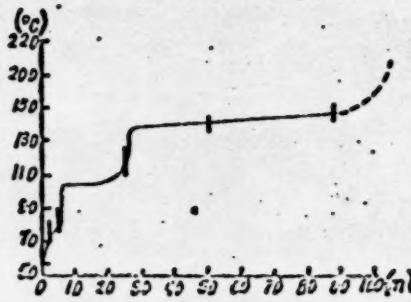

Fig. 4. Fractionation curve of the aromatic part (together with unsaturated hydrocarbons) of the ethylcyclohexane catalyzate.

Table 7 gives the values of the degrees of conversion of the cycloalkanes that we have studied, and it gives also the yields of aromatic hydrocarbons formed from the cycloalkanes in the catalytic treatment.

TABLE 7

Reactions of Cycloalkanes in Contact with Activated Troshkov Clay

Hydrocarbon	Degree of conversion (% by weight on original hydrocarbon)	Amount of aromatics (% on original hydrocarbon)
Cyclopentane	10-12	1
Cyclohexane	11-12	3
Ethylcyclopentane	26-28	17
Methylcyclohexane	30-32	11
Ethylcyclohexane	40-41	22

It will be seen from Table 7 that the degree of the conversion of the cycloalkane and the yield of aromatic hydrocarbons rise as the molecular weight rises.

Contact-catalysis Reactions of Ethylbenzene

Ethylbenzene was passed in 50-ml (43.4-g) portions. The properties of the ethylbenzene catalyzates are given in Table 8.

Analysis of gas	
Unsaturated hydrocarbons	9.8%
Hydrogen	82.8%
Paraffin hydrocarbons	7.4%

The fractionation curve for the combined catalyzate from the two experiments fractionated through a 20-plate column is given in Fig. 5. For the fractionation 70.0 g of catalyzate was taken. The yields and properties of the fractions of the catalyzate are given in Table 9.

TABLE 8

Properties of Ethylbenzene Catalyzates

Expt. no.	Yield of catalyzate (%)	Yield of gas (liter, NTP)	Properties of catalyzate			
			n_D^{20}	d_4^{20}	Content of sulfonatable hydrocarbons (% by volume)	Iodine number
1	94.0	1.528	1.4977	0.8700	98.0	2.8
2	95.0	1.435	1.4975			

TABLE 9

Properties of Fractions of the United Ethylbenzene Catalyzate

Fraction no.	Boiling range (°C)	Yield		Properties of the fraction			
		(g)	(% by weight)	n_D^{20}	d_4^{20}	Bayer test	Iodine number
I	78.1 – 83.1	3.0	4.3	1.4983	0.8756	Negative	–
II	83.1 – 136.0	61.7	89.3	1.4960	0.8666	Negative	–
III	136.0 – 200	4.0	5.7	1.5215	0.9030	Positive	27.5
Residue		0.4	0.6	1.5300	–	–	–

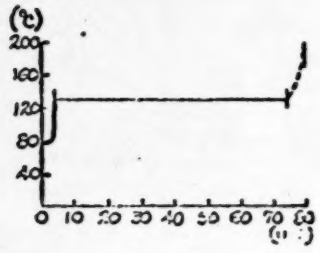

Fig. 5. Fractionation curve of the ethylbenzene catalyzate.

It will be seen from Table 9 and the fractionation curve that, under the given conditions, ethylbenzene yielded 4.3% of benzene (Fraction I) and 5.8% of higher aromatic hydrocarbons admixed with a small amount of unsaturated hydrocarbons (Fraction III). Fraction II consisted mainly of unchanged ethylbenzene admixed with very small amounts of benzene. Thus, ethylbenzene, like toluene, was very stable under the catalytic treatment: 89% of it remained unchanged.

If the dehydrogenation of ethylcyclohexane had occurred more rapidly than the synthesis from it of new alkyl-substituted cyclohexanes (mainly methyl derivatives), then the catalyzate would have consisted mainly of ethylbenzene. Actually, however, ethylbenzene was detected only qualitatively in the ethylcyclohexane catalyzate. Hence, under the given conditions, the synthesis of new alkyl-substituted cyclohexanes was more rapid than the dehydrogenation of the original ethylcyclohexane.

SUMMARY

1. A study has been made of the reactions of cyclopentane, ethylcyclopentane, ethylcyclohexane, and ethylbenzene in contact with activated Troshkov clay at 500°.

2. It has been established that the degree of conversion of cycloalkanes increases with increase in molecular weight. For cyclopentane the degree of conversion is 10-12%, for ethylcyclopentane it is 26-28%, and for ethylcyclohexane it is 40-41%.

3. On the basis of a comparative study of the behavior of ethylcyclohexane and ethylbenzene it is suggested that under the given catalysis conditions, reactions leading to the synthesis of alkyl derivatives are more rapid than the dehydrogenation of the original ethylcyclohexane.

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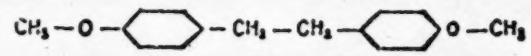
PHOTODEHYDROCONDENSATION OF ANISOLE HOMOLOGS. PHOTOSYNTHESIS OF SYNESTROL

B. M. Mikhailov and A. N. Blokhina

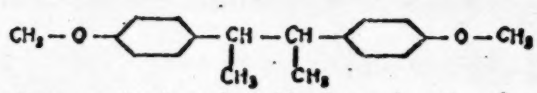
Under the influence of sunlight benzene homologs react with ketones with formation of compounds of two types, alcohols and hydrocarbons. Thus, by prolonged insolation of a mixture of toluene and benzophenone, Ciamician and Silber [1] have obtained bibenzyl and 1,1,2-triphenylethanol. When irradiated, ethylbenzene and benzophenone gave a hydrocarbon and an alcohol, and also benzopinacol [2]. The structures of the hydrocarbon and the alcohol were not established, but the composition of the hydrocarbon ($C_{16}H_{18}$) suggests that it could be 1,4- or 2,3-diphenylbutane. Other benzene homologs (p-propybenzene and p-xylene) give similar reactions.

We have investigated the photochemical reactions of anisole homologs in presence of acetone, the mixture of reactants being exposed to ultraviolet radiation and we have found that, under these conditions, para homologs of anisole undergo photodehydrocondensation reactions and yield methoxyphenyl derivatives of aliphatic hydrocarbons.

p-Methylanisole yielded 4,4'-dimethoxybibenzyl (I). p-Ethylanisole underwent condensation at its α-carbon atoms and yielded 4,4'-dimethyoxy-α,α'-dimethylbibenzyl (II):

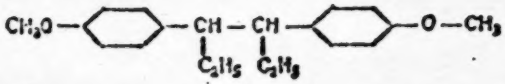


(I)



(II)

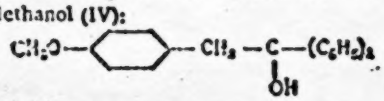
This view of the course of the latter reaction is confirmed by the condensation of p-propylanisole, in which reaction was undoubtedly at the α-carbons, the product being α,α'-diethyl-4,4'-dimethoxybibenzyl (III):



(III)

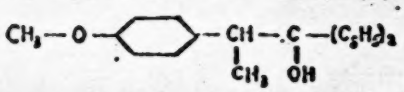
which was readily hydrolyzed to synestrol (α,α'-diethyl-α,α'-dihydrostilbestrol, or 4,4'-(1,2-diethylethylene), a synthetic female sex hormone of high activity.

When a mixture of p-methylanisole and benzophenone was irradiated in acetone solution, not only 4,4'--dimethoxybibenzyl was formed, but also the product of the condensation of p-methylanisole with benzophenone, 2-(p-methoxyphenyl)-1,1-diphenylethanol (IV):



(IV)

When p-ethylanisole was irradiated under similar conditions, an alcohol was obtained. This product was evidently 2-(p-methoxyphenyl)-1,1-diphenyl-1-propanol (V):



(V)

EXPERIMENTAL

Starting Materials. p-Methylanisole was prepared by the methylation of p-cresol and boiled at 75-77° (22 mm) [3]. p-Ethylanisole, b.p. 112° (46 mm), was prepared by the methylation [3] of p-ethylphenol, which was itself prepared by the reduction [4] of 4'-hydroxyacetophenone [5]. In order to obtain p-propylanisole (b.p. 211-212°), anisole was condensed with propionyl chloride [6], and the resulting 4'-methoxypropionophenone was subjected to Clemmensen reduction [7].

All experiments were carried out in quartz flasks hermetically closed with corks. The air was displaced from the reaction vessels with nitrogen. A PRK-4 quartz lamp was used as a source of ultraviolet radiation. The reaction vessels were placed at a distance of 30 cm from the lamp.

4,4'-Dimethoxybibenzyl. A mixture of 30 ml of p-methylanisole and 40 ml of acetone was irradiated for 230 hours. Acetone and p-methylanisole were distilled off, and the oily reside (1.45 g) partially crystallized when treated with ethanol. The substance obtained (0.09 g) was crystallized from ethanol and formed long colorless plates, m.p. 129-130°. The reported melting point of 4,4'-dimethoxybibenzyl is 128.5-130° [8].

	Found %:	C 79.60; H 7.62
$C_{16}H_{18}O_2$.	Calculated %:	C 79.29; H 7.49

4,4'-Dimethoxy-α,α'-dimethylbibenzyl. A mixture of 20 ml of p-ethylanisole and 35 ml of acetone was irradiated for 200 hours. After removal of acetone at atmospheric pressure and p-ethylanisole at 6 mm Hg, 1.56 g of an oily residue was obtained. Treatment of this with methanol yielded a crystalline substance (0.08 g), which after crystallization from the same solvent melted at 136-136.5° and which corresponded in analysis to 4,4'-dimethoxy-α,α'-dimethylbibenzyl.

	Found %:	C 79.83 H 8.31
$C_{18}H_{22}O_2$	Calculated %:	C 79.95 H 8.20

α,α'-Diethyl-4,4'-dimethoxybibenzyl (Dimethyl Ether of Synestrol). A mixture of 20 ml of p-propylanisole and 35 ml of acetone was irradiated for 235 hours. Acetone was then driven off from a water bath, and the unchanged p-propylanisole was distilled off under reduced pressure. The oily residue (1.34 g) was dissolved in methanol, and 0.04 g of a substance melting at 124-130° crystallized out. After recrystallization from a mixture of acetone and methanol, the substance formed colorless plates (0.02 g) melting at 141-145°. The melting point was not depressed by admixture of synthetic dimethyl ether of synestrol (m.p. 143.5-144° [9]).

	Found %:	C 80.67; H 8.73
$C_{20}H_{26}O_2$	Calculated %:	C 80.48; H 8.79

2-(p-Methoxyphenyl)-1,1,-diphenylethanol. A mixture of 10 ml of p-methylanisole, 15 g of benzophenone, and 15 ml of acetone was irradiated for 240 hours. Unchanged starting materials were removed by distillation, and a residue of 2 g remained which did not distil below 185° at 14 mm. It was dissolved in ethanol, and 0.81 g of a substance melting at 129-137° crystallized out. Two recrystallizations from the same solvent yielded needles melting at 141-142.5° The substance corresponded in analysis to 2-(p-methoxyphenyl)-1,1-diphenylethanol.

	Found %:	C 82.91; H 6.72
$C_{21}H_{20}O_2$	Calculated %:	C 82.85; H 6.62

The main mother liquor was evaporated down, and the residue was dissolved in a mixture of benzene and n-hexane (1 : 1) and subjected to chromatographic analysis on alumina (20 g). The first fraction (150 ml) contained a substance which, after crystallization from alcohol, had a melting point of 129-130°, undepressed by admixture of a sample of 4,4'-dimethoxybibenzyl. By elution of a second fraction with a mixture of benzene and alcohol (1 : 1), a further 0.43 g of 2-(p-methoxyphenyl)-1,1-diphenylethanol, m.p. 137-140° (from alcohol) was isolated.

2-(p-Methoxyphenyl)-1,1-diphenyl-1-propanol. A mixture of 10 ml of p-ethylanisole, 13 g of benzophenone, and 20 ml of acetone was irradiated for 110 hours. The residue (5 g) obtained after removal of unchanged starting materials was dissolved in a mixture of benzene and n-heptane (1 : 6) and subjected to chromatographic analysis on alumina. At first, elution was effected with a mixture of the same solvents in the same proportions. The first fraction (250 ml) contained a crystalline substance, but we did not succeed in purifying this completely. Elution was continued with a 1 : 1 mixture of benzene and heptane, and the substance then isolated was crystallized from alcohol. It melted at 107-108°, and corresponded in analysis to 2-(p-methoxyphenyl)-1,1-diphenyl-1-propanol.

	Found %:	C 82.87; H 6.92
$C_{22}H_{22}O_2$	Calculated %:	C 82.97; H 6.96

SUMMARY

1. When exposed to ultraviolet radiation in presence of acetone, para anisole homologs undergo dehydrocondensation with formation of p-methoxyphenyl derivatives of aliphatic hydrocarbons. In particular, synestrol can be obtained by this method from p-propylanisole.

2. When these reactions are carried out in presence of benzophenone, in addition to dehydrocondensation products it is possible to isolate 2-(p-methoxyphenyl)-1,1-diphenyl-1-alkanols, formed by the condensation of the para anisole homologs with the ketone.

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ABSORPTION SPECTRA AND MOLECULAR STRUCTURE*

COMMUNICATION 3. MODERN ELECTRONIC THEORY, AND THE COLOR OF ARYLHYDRAZONES OF 9-ACRIDINECARBOXALDEHYDE

A. A. Kharkharov

An open discussion on problems of chemical structure has revealed that the concept of resonance is scientifically unsound, and it has directed the work of Soviet chemists along the lines of the further evolution of the teaching of Butlerov and Markovnikov. It has shown the great significance, as a modern interpretation of teaching relating to the mutual effects of atoms and groups of atoms, of the electronic theory that is being developed in organic chemistry by Soviet investigators.

For the experimental verification of hypotheses based on electronic theory in its application to the color of organic compounds, we have used data derived from spectrum investigations of arylhydrazones of 9-acridinecarboxaldehyde [1]. Hydrochlorides of 9-acridinecarboxaldehyde arylhydrazones behave as typical dyes; not only are they deeply and intensely colored, but they are able to dye textile fibers. The powerful bathochromic effect that we observe as we pass from the hydrazone bases to their salts is to be explained by the enhanced electron-accepting properties of the acridine nitrogen, due to the addition of a proton at its free electron pair, and the consequent marked change in the positions of all energy levels of the molecule. The effect of the group extends over the whole molecule. Raising of the ground-state energy level of the molecule is accompanied by a deepening of color, for it is usually found that, when the energy levels are higher, they are closer together. The higher the ground state of a molecule, the less is the change in energy in an electron transition from the ground state to an excited state. This effect can be seen when we compare the color of 9-acridinecarboxaldehyde phenylhydrazone (λ_{max} 465 mμ) (Fig. 1.):

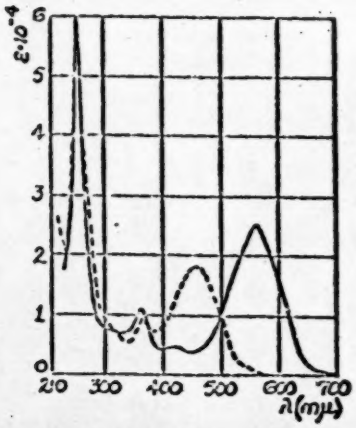
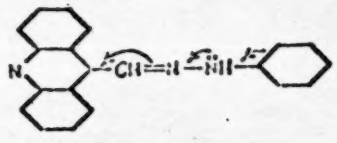
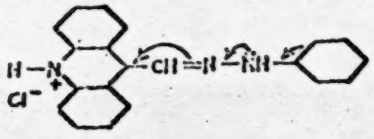


Fig. 1. Absorption spectra of 9-acridinecarboxaldehyde phenylhydrazone: ——— dissolved in alcoholic hydrogen chloride; – – – dissolved in alcohol.



(Yellow)

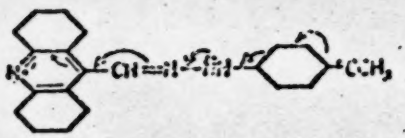
with that of its hydrochloride (λ_{max} 562 mμ) (Fig. 1):



(Reddish violet)

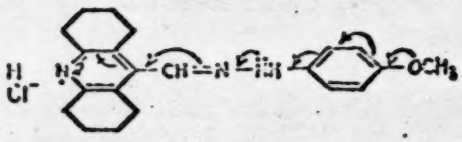
The difference in the positions of the maxima of the principal absorption bands is still greater for 9-acridinecarboxaldehyde p-methoxyphenylhydrazone (λ_{max} 470 mμ):

*Work performed in fulfilment of requirements for the doctorate of the Institute of Organic Chemistry of the USSR Academy of Sciences.



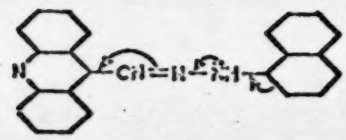
(Yellowish brown)

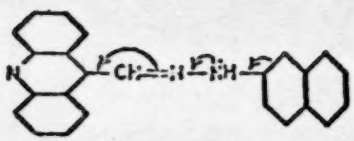
and its salt (λ_{max} 610 mμ):



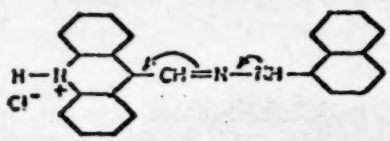
(Greenish blue)

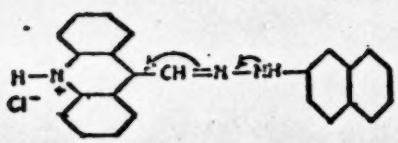
and also for the bases:



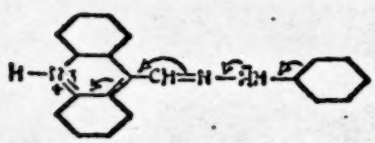


and salts of 9-acridinecarboxaldehyde naphthylhydrazones (Fig. 2 and 3):





On the basis of an examination of the electronic structure of the cation of 9-acridinecarboxaldehyde phenylhydrazone:



we suggested, and confirmed experimentally, that the introduction of electron-donating substituents, such as an acetamido group para to the positively charged nitrogen of the acridine ring system, would result in partial neutralization of this charge. The resulting weakening of the electron-accepting power of the nitrogen is accompanied by a reduction in the diplacement of electrons from the phenyl nucleus to the heterocycle, and so by a shift in the principal absorption maximum towards the short waves. Thus, as we pass from the hydrochloride of

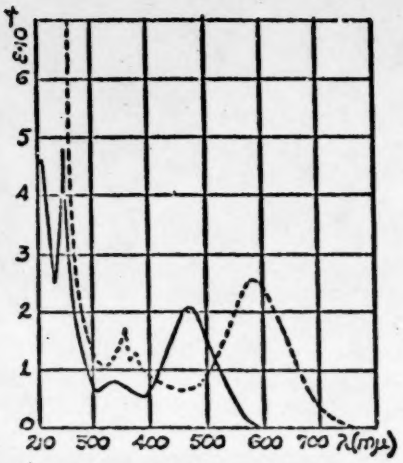


Fig. 2. Absorption spectra of 9-acridinecarboxaldehyde 1-naphthylhydrazone; – – – dissolved in alcoholic hydrogen chloride; ——— dissolved in alcohol.

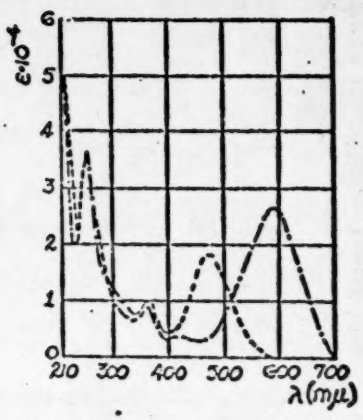
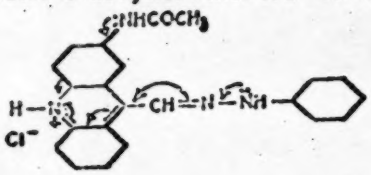
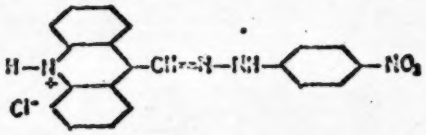


Fig. 3. Absorption spectra of 9-acridinecarboxaldehyde 2-naphthylhydrazone; –·–·–, dissolved in alcoholic hydrogen chloride; – – – dissolved in alcohol.

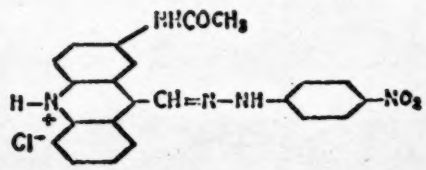
9-acridinecarboxaldehyde phenylhydrazone to the hydrochloride of 2-acetamido-9-acridinecarboxaldehyde:



the principal maximum is displaced from 562 to 512 mμ (Fig. 4, Table 1), and as we pass from the hydrochloride of 9-acridinecarboxaldehyde p-nitrophenylhydrazone:



to the hydrochloride of 2-acetamido-9-acridinecarboxaldehyde p-nitrophenylhydrazone:



the displacement is from 522 to 375 mμ (Fig. 4, Table 1).

Our investigations have thus shown that one of the postulates of the chromophore theory [2], i.e. that the introduction of auxochromic groups results in a deepening of color, is not always true. In the examples examined the introduction of auxochromic groups does not deepen the color, but lightens it.

The theory of electron displacements have enabled us to predict also that the presence of electron-donating substituents in the phenyl nucleus will act synergically with the positively charged nitrogen in bringing about electron displacements directed through the system from the substituent via the phenyl nucleus and the –NH–

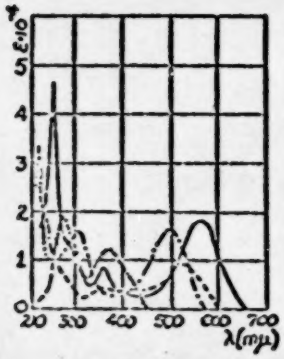


Fig. 4. Absorption spectra in alcoholic hydrogen chloride solutions: 9-acridinecarboxaldehyde phenylhydrazone; – – – 9-acridinecarboxaldehyde p-nitrophenylhydrazone; –·–·–·– 2-acetamido-9-acridinecarboxaldehyde phenylhydrazone; ····· 2-acetamido-9-acridinecarboxaldehyde p-nitrophenylhydrazone.

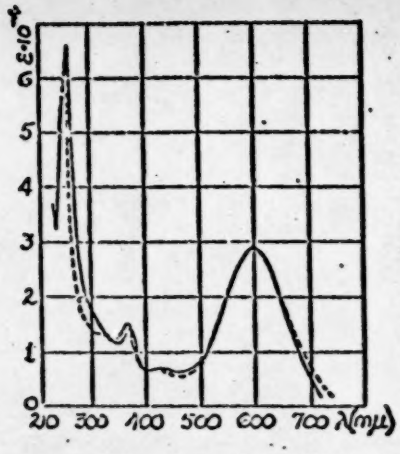
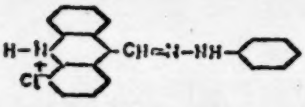
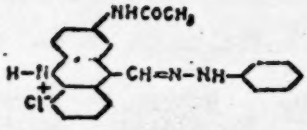
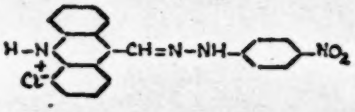
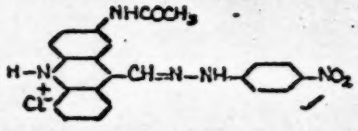
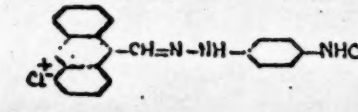


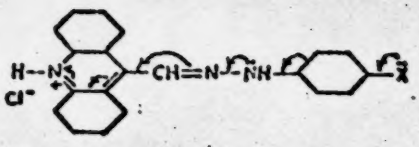
Fig. 5. Absorption spectra of alcoholic hydrogen chloride solutions: – – – 9-acridinecarboxaldehyde p-acetamidophenylhydrazone; ——— 9-acridinecarboxaldehyde p-benzamidophenylhydrazone.

TABLE 1

Absorption Maxima of Alcoholic Hydrogen Chloride Solutions of Acetamido Derivatives of 9-Acridinecarboxaldehyde Phenylhydrazone

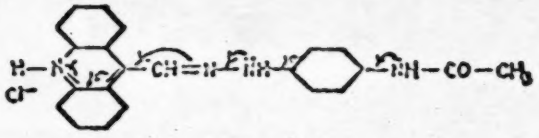
Substance	Formula	Absorption maxima (mμ)		
		1	2	3
Hydrochloride of 9-acridinecarboxaldehyde phenylhydrazone		254	364	562
Hydrochloride of 2-acetamido-9-acridinecarboxaldehyde phenylhydrazone			314	512
Hydrochloride of 9-acridinecarboxaldehyde p-nitrophenylhydrazone		256	364	522
Hydrochloride of 2-acetamido-9-acridinecarboxaldehyde p-nitrophenylhydrazone			278	375
Hydrochloride of 9-acridinecarboxaldehyde p-acetamidophenylhydrazone		256	366	598

group to the nitrogen of the acridine ring system:



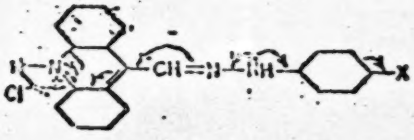
The action of electron-donating substituents is to effect a greater change in the electron densities of all atoms of the system, as compared with the changes in unsubstituted 9-acridinecarboxaldehyde phenylhydrazone, and so to deepen the color.

Thus, if we again introduce the acetamido (or benzamido) group into the unsubstituted compound, i not in position 2 in the acridine ring system, but in the phenyl group e.g. para to the —NH— group, there is now a lightening of the color, not deepening, (λ_{max} 598 mμ; Fig. 5, Table 1).



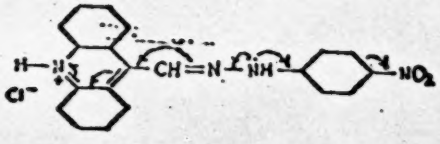
It will be seen that the same substituent, depending on its position in the molecule, may either deepen or lighten the color. This shows that conclusions made on the basis of electronic theory are in accord with experiment, i.e. with practice. All that we have stated concerning auxochromes may be extended also to chromophores.

Electron-accepting groups oppose the tendency of the positively charged nitrogen to attract electrons:



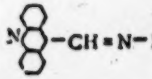
and in this way reduce the disturbances in electron density and lighten the color.

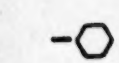
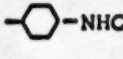
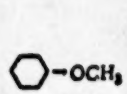
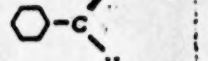
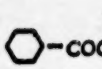
In the present case such electron-accepting substituents as NO_2, CHO, $COCH_3$, which are usually regarded as typical chromophores, do not deepen, but lighten the color. For example, the principal absorption maximum of the hydrochloride of 9-acridinecarboxaldehyde p-nitrophenylhydrazone:

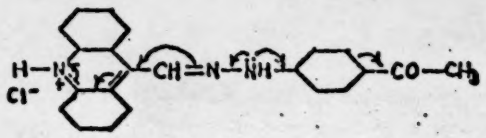


is displaced towards the short waves by 40 mμ, as compared with the unsubstituted compound (Fig. 4, Table 1), and the maximum of the hydrochloride of the p-acetylphenylhydrazone of the same aldehyde:

TABLE 2

Principal Properties of Aryl-hydrazones of 9-acridinecarboxaldehyde  (Abbreviations: y = yellow; g = green; r = red; br = brown; o = orange; v = violet; d = dark)

Compound	R	M.p. (°C)	Color of dry substances		Color of solutions					Principal absorption maximum (mμ)			Color of dyeing on silk
			free	salt	in aqueous alcoholic caustic soda	in alcohol	in alcoholic caustic soda	in concentrated sulfuric acid	in glacial acetic acid	in alcohol	in 0.2 N alcoholic HCl	in aqueous alcoholic caustic soda	in alcoholic caustic soda	
9-Acridinecarboxaldehyde phenylhydrazone		215	br–y	v–black	y	y	y–g	br–y	v–r	460	562	560	640	r–v
9-Acridinecarboxaldehyde p-acetamidophenyl hydrazone		120	br	g	br	br	br	r–v	blue	–	599	600	–	blue
9-Acridinecarboxaldehyde p-methoxyphenyl hydrazone		182	d–br	d–blue	br–y	br–y	gray-g	y–br	g-blue	470	610	610	–	g–blue
9-Acridinecarboxaldehyde p-formylphenyl hydrazone		138	br	g	o	o	g–blue	y–r	r–v	–	539	540	–	v–r
9-Acridinecarboxaldehyde p-acetylphenyl-hydrazone		201	br	g	y–br	y–br	g–blue	r	v–r	–	540	540	–	v–r
9-Acridinecarboxaldehyde p-nitrophenyl-hydrazone		252	y	g	y	y	blue	o	r	444	522	520	630	blue–r
9-Acridinecarboxaldehyde 1-naphthylhydrazone		195	br	r-black	br	y	br–y	br	blue	467	595	595	–	blue
9-Acridinecarboxaldehyde 2-naphthylhydrazone		207	br	r-black	br	y	g	br	blue	470	592	590	–	blue



is displaced in the same direction by 22 mμ (Fig. 4, Table 1). Hence, not only auxochromes, but also chromophores may, depending on their positions in the molecule, either deepen or lighten the color.

These phenomena, which are predicted by the theory of electron displacements, cannot be explained, and certainly cannot be predicted, either by the chromophore theory [2], by the quinonoid theory [3, 4], or by the coordination theory [5-9].

It should be noted that the quinonoid theory is not only unable to explain the effect of substituents, but is unable also to explain color of 9-acridinecarboxaldehyde phenylhydrazone itself, since its molecule does not have a quinonoid structure. Moreover, Dilthey and Wizinger's theory of coordinative unsaturation is found to be unsound when the effect of the identity and disposition of the substituents is examined. The examples that we have given, therefore, enable us to form a judgement of the greater validity and power of prediction of the theory of electron displacements, as compared with pre-electronic theories of color, including the chromophore theory.

We have now shown, and we shall later illustrate for dyes widely used in practice, that the chromophore theory, which has been borne out by a considerable amount of experimental material and has done great service to chemistry and to the synthetic dye industry is in conflict with practical observations in a number of cases. It is necessary, therefore, to reexamine the chromophore theory from the point of view of electronic theory. In other words, it must be introduced in a more precise form into the theory of electron displacements, so as to form a component part of this theory. The same may be said of the other theories of color. Those postulates of the other theories that are in accord with practice must be taken into account in modern electronic theory. Electronic theory, as applied by us in the establishment of the relation between color and structure in organic compounds, is being developed by many Soviet investigators [10-15].

With the aid of Butlerov's theory of structure, supplemented by electronic theory, "we" as Izmailsky writes [12], "can give an approximate expression of the actual structure with the aid of a single formula, using the conjugation symbol". In Izmailsky's words: electronic formulas are formulas of fine structure - they provide a second degree of approximation to objective reality. Here lies the explanation of the greater cognitive possibilities of electronic theory, as compared with all previous theories.

EXPERIMENTAL

The arylhydrazones of 9-acridinecarboxaldehyde were prepared by the method already described by us [1, 15-19]. Their principal properties are given in Table 2. All spectrum investigations were carried out with an SF-1 photoelectric spectrophotometer. Before the measurements were made, the substances were carefully purified, and their purities were checked by analysis (Table 3).

TABLE 3

Analyses of Arylhydrazones of 9-Acridinecarboxaldehyde

Compound	Elementary composition	Molecular weight	Nitrogen content (%)	
			Found	Calculated
9-Acridinecarboxaldehyde phenylhydrazone	$C_{20}H_{15}N_3$	297	14.36	14.14
9-Acridinecarboxaldehyde p-acetamidophenylhydrazone	$C_{22}H_{18}N_4O$	354	15.54	15.82
9-Acridinecarboxaldehyde p-methoxyphenylhydrazone	$C_{21}H_{17}N_3O$	327	12.96	12.84
9-Acridinecarboxaldehyde p-formylphenylhydrazone	$C_{21}H_{15}N_3O$	325	13.25	12.96
9-Acridinecarboxaldehyde p-acetylphenylhydrazone	$C_{22}H_{17}N_3O$	339	12.55	12.39
9-Acridinecarboxaldehyde p-nitrophenylhydrazone	$C_{20}H_{14}N_4O_2$	324	16.34	16.37
9-Acridinecarboxaldehyde 1-naphthylhydrazone	$C_{24}H_{17}N_3$	347	12.65	12.10
9-Acridinecarboxaldehyde 2-naphthylhydrazone	$C_{24}H_{17}N_3$	347	12.29	12.10

SUMMARY

1. On the basis of electronic theory it is predicted, and shown experimentally, that a given substituent, depending on its position in the molecule, may either deepen or lighten the color.

2. Examples are given that illustrate the greater validity and power of prediction of electronic theory, as compared with pre-electronic theories of color.

3. It is emphasized that electronic theory does not displace the old pre-electronic theories of color, but lends precision to them and unifies them within itself.

4. The properties of five arylhydrazones of 9-acridinecarboxaldehyde are described for the first time.

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SOME PHYSICO-MECHANICAL PROPERTIES OF ESTERS OF POLYVINYL ALCOHOL

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Although vinyl ester polymers are now of great technological importance, there is very little information in the literature about their physico-mechanical properties. Also, most of the available data relate to fully substituted polyvinyl acetate, whereas not only the polyvinyl acetate prepared by direct polymerization of the monomer is of importance, but also partially substituted products, which may be regarded as copolymers of vinyl alcohol with vinyl acetate. The properties of such partially hydrolyzed polyvinyl acetates, and also the physico-mechanical properties of polymers of the vinyl esters of acids other than acetic, have remained almost without investigation.

The objects of our investigation included the characterization of the main physico-mechanical properties of the most important polyvinyl esters: polyvinyl formate, acetate, propionate, and butyrate of various degrees of substitution. As our main physical criteria for the appraisal of the fundamental properties of the polymers, we have selected a) the vitrification temperature T_v, and b) the tensile strength, elasticity modulus, and extension at break for two states of the polymer: vitreous, at 40° below T_v, and highly elastic, at 10° above T_v. As is well known, these criteria are of fundamental importance for the characterization of the properties of polymers. The vitrification temperature T_v is almost independent of chain length, since it is associated only with the movement of separate units of the chain. The mechanical strength of polymers is insignificant for a degree of polymerization of less than 40-80, but it then begins to increase, approximately in proportion to the increase in chain length, until the degree of polymerization reaches about 250; the curve for this relationship then bends over, and for a degree of polymerization of greater than about 600, further increase in chain length is almost without effect on the properties of the polymer. The degree of polymerization of polyvinyl esters, as generally prepared, is often less than 600, and to obtain comparable results in the determination of mechanical properties, the polymers examined must have approximately the same degree of polydispersity. We have prepared such polymers from polyvinyl alcohol by careful esterification under mild conditions [1].

For the preparation of highly substituted polyvinyl formate, we have used the method of repeated esterification with formic acid [2]. Partially formylated polyvinyl alcohols were prepared by esterification with aqueous solutions of formic acid of various concentrations. Acetic, propionic, butyric, and isobutyric esters of polyvinyl alcohol were prepared by the action of the corresponding acid anhydrides on polyvinyl alcohol in a pyridine medium. Partially esterified polyvinyl alcohols were prepared by partial hydrolysis or alkaline alcoholysis of the full esters.

In order to verify that no appreciable chain degradation had occurred during the esterification of polyvinyl alcohol and the partial saponification of polyvinyl esters under our conditions, we compared the intrinsic viscosities of the original polyvinyl alcohol and the polyvinyl alcohol regenerated by complete hydrolysis of the ester prepared from it. The intrinsic viscosities of all samples of polyvinyl alcohol regenerated in this way in our experiments were within the range 0.72-0.78, the value for the original polyvinyl alcohol being 0.74. It should be remembered that these viscosity figures refer to substances that have received a double treatment — esterification of polyvinyl alcohol, and hydrolysis of the resulting ester — whereas the esters under comparison in our investigation were prepared by one operation (esterification) from a single sample of polyvinyl alcohol.

EXPERIMENTAL

As stated above, in the study of the physico-mechanical properties of esters of polyvinyl alcohol, we have used samples of polyvinyl formate, acetate, propionate, butyrate, and isobutyrate varying in degree of substitution.

Determination of the Vitrification Temperature. The determination was carried out by two methods. As our basic method we used the dilatometric method, which gives the most accurate results, but for some samples supplementary tests were done in a Martens apparatus.

For the determination of the vitrification temperature the polymers were compressed into disks 3-4 mm thick and 1 cm in diameter, and each disk was then cut into two semicircular pieces. The compression was carried out at 40-50° above the estimated vitrification temperature, and a pressure of 50-60 kg/sq. cm was maintained for ten minutes. After a determination had been made with this sample, further determinations could be made with a more precise compression temperature. The dilatometer, containing the polymer sample immersed in mercury, was placed in a bath having a temperature 10-20° lower than the expected vitrification temperature, and was kept there for some time. The temperature was then raised at a rate of 2° in ten minutes, and readings were taken of

the level of mercury in the capillary. A curve was plotted for the dependence of the mercury level V in the capillary on the temperature t, and the temperature at which a break occurred in the straight line representing the dependence of V on t was taken to be the vitrification temperature. Duplicate determinations were always in good agreement.

The results of the determinations of the vitrification temperatures of polyvinyl esters varying in degree of substitution are summarized in Table 1 and Fig. 1. In individual cases we determined T_v not only dilatometrically but also by means of the Martel apparatus. The apparatus and procedure are described in Reikh and Fainberg's book [3]. This apparatus was designed for the determination of T_v for rubbers, but we have used it successfully for the determination of the vitrification temperatures of plastics. The test sample was a compressed cylinder, diameter 0.5 cm and height 0.6-0.7 cm. The results of these tests are given in Table 2.

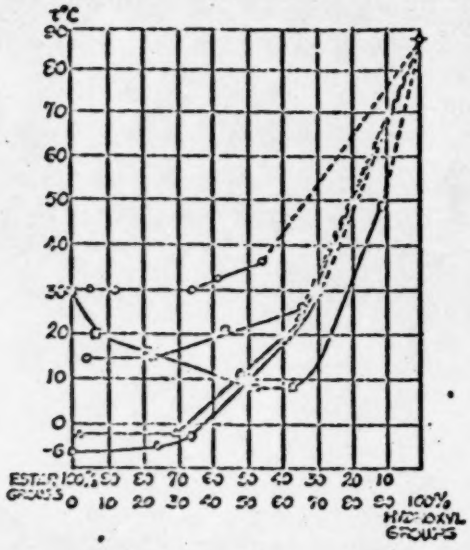

Fig. 1. ◇ - polyvinyl alcohol; □ - formic ester; O - acetic ester; Δ - propionic ester; ● - butyric ester; ⊙ - isobutyric ester.

Preparation of Films. The mechanical properties of the polyvinyl esters were determined on films. The films were cast from a 5-10% solution — on glass for polyvinyl alcohol, and on the surface of mercury for all the other polymers. The composition of the solvent was chosen according to the degree of esterification and the identity of the ester group (Table 3). In the preparation of films of polyvinyl formates some of the ester groups were hydrolyzed off by atmospheric moisture and by water contained in some of the solvent mixtures (Table 4).

In order to obtain films free from strain, it is recommended [4] that the films should be formed in an atmosphere saturated in solvent vapor. Particularly high strains arise in films cast from solutions containing a nonsolvent that evaporates more slowly than the solvent.

TABLE 1

Dependence of the Vitrification Temperatures * of Polyvinyl Esters on their Ester-group Contents

Polyvinyl formate		Polyvinyl acetate		Polyvinyl propionate		Polyvinyl butyrate		Polyvinyl isobutyrate	
Content of ester groups (mole-%)	T_v	Content of ester groups (mole-%)	T_v	Content of ester groups (mole-%)	T_v	Content of ester groups (mole-%)	T_v	Content of ester groups (mole-%)	T_v
100**	30	100***	30	98.5	−2	100.0	−6	96.7	15
99.2	30	96.5	30	72.6	−2	76.0	−4	77.0	15
93.6	20	66	30	53.4	11	67.0	−1	56.0	22
78.0	17	58.5	33	34.7	23	30.0	30	34.7	25
48.0	9	45.5	35						
36.3	9								
10.0	49								

* Vitrification temperatures were determined in a dilatometer.

** Polyvinyl formate prepared by the polymerization of vinyl formate.

*** Polyvinyl acetate prepared by reacetylation of polyvinyl alcohol.

In our work water acted as a nonsolvent of this sort. When a film was cast, as described above, and a part of the solvent allowed to evaporate, coagulation generally set in. For this reason, the bath of mercury covered with polymer solution was placed in a desiccator containing calcium chloride. Under these conditions the removal of water from the solution was fairly rapid, and the solution did not coagulate. Films of polyvinyl butyrate containing less than 67 mole-% of ester groups were found to be very elastic. Before these films were cast, a metal frame was

placed on the mercury surface, and the film was taken from the surface in this frame and vacuum-dried, and only then was it cut from the frame. After removal from the mercury, the films were vacuum-dried to constant weight under conditions similar to the original drying of these polymers. After being dried, all of the films were kept in a vacuum desiccator over calcium chloride.

TABLE 2
Dependence of the Vitrification Temperatures* of Polyvinyl Esters on their Ester-group Contents

Polyvinyl formate		Polyvinyl acetate	
Content of ester groups (mole-%)	T_v	Content of ester groups (mole-%)	T_v
99.8	28	100	30
78.0	19	88	30
36.0	7	70	28

* Vitrification temperatures were determined in the Marei apparatus.

Apparatus for Testing the Films. The films were tested in a modified form of the apparatus used for determining the stability of rubber to frost [5]. The results of the tests are given in Table 5.

The following conclusions can be drawn from the foregoing results. As was to be expected, T_v is independent of the method of preparing the polyester. Values previously reported [6] for the vitrification temperatures of polyvinyl acetate and polyvinyl alcohol are 28° and 85° respectively, and we have obtained the values of 30° and 85°. No values of T_v have been reported in the literature for the other polymers that we have investigated. The unexpected coincidence of the vitrification temperatures of polyvinyl acetate and polyvinyl formate, and also the unusual course of the variation of T_v for polyvinyl formates with variation in formyl content, led us to check the values of T_v for these polymers in a Marei apparatus.

TABLE 3
Solvents Used in the Casting of Films

Polyvinyl acetate		Polyvinyl propionate		Polyvinyl butyrate		Polyvinyl isobutyrate	
Content of ester groups (mole-%)	Solvent	Content of ester groups (mole-%)	Solvent	Content of ester groups (mole-%)	Solvent	Content of ester groups (mole-%)	Solvent
100.0	Acetone	98.5	Ethanol	100.0	Ethanol	96.7	Ethanol
70.8	Acetone	72.6	30% Aqueous ethanol	76.4	Ethanol	77.0	Ethanol
66.0	90% Aqueous acetone	53.4	17% Aqueous ethanol	67.0	90% Aqueous ethanol	56.0	85% Aqueous ethanol
58.5	50% Aqueous acetone	34.7	25% Aqueous ethanol	35.4	50% Aqueous ethanol	34.7	60% Aqueous ethanol
45.5	66% Aqueous acetone						

TABLE 4
Degree of Hydrolysis and Content of Formic Ester Groups in Polyvinyl Formate Films after Drying

Content of ester groups before the casting of the film (mole-%)	Solvent	Content of ester groups in film (mole-%)	Proportion of hydrolyzed ester groups (mole-%)
96.6	Acetone	88.0	8.6
78.0	Acetone	69.0	9.0
68.7	(75% aqueous acetone)	60.0	8.7
48.0	(80% aqueous pyridine)	28.0	20.0
36.3	50% aqueous acetone	18.3	13.0

In the Marei apparatus, T_v is taken as the temperature at which highly elastic deformation appears. As the strain on the sample during the test is very slight (almost zero), the values of T_v determined in the dilatometer and in the Marei apparatus should coincide.

It will be seen from Table 6 that there is fairly good agreement between the values of T_v determined for these polymers by the two methods.

The vitrification temperatures of the full esters formed by polyvinyl alcohol with the normal fatty acids (excluding formic acid) fall as the size of the hydrocarbon part of the acid increases. It should be noted that the difference in the values of T_v for the acetic and propionic esters (32°) is much greater than that for the propionic and butyric esters (4°). The variations observed in T_v as we pass from polyvinyl alcohol to its esters and from one kind of ester side group to another may be explained as follows.

As is well known, the vitrification temperature depends on the extent of interaction between the polymer chains. Intermolecular forces are made up of the interactions of the atoms of the main chains and the interactions of the atoms

of the side groups. In polyvinyl alcohol, Van der Waals forces act between main-chain carbons, and powerful hydrogen bonding occurs between the hydroxyl side groups. It has been calculated that the energy of molecular interaction of a polyvinyl alcohol chain 5 A in length and having a coordination number of 4 (i.e. each chain surrounded by four other chains) amounts to 4200 kcal.

TABLE 5

Physico-mechanical Properties of Polyvinyl Esters

Ester	Content of ester groups (mole-%)	Temp. of test (°C)	Tensile strength p (kg/cm²)	Elastic modulus E (kg/cm²)	Extension at break (%)	Temp. of test (°C)	Tensile strength p (kg/cm²)	Elastic modulus E (kg/cm²)	T_v, determined dilatometrically
Polyvinyl formate	100	40	63	2	2,100	−10	400	7,000	30
	88	23	76	2	1,550	−20	620	7,500	18
	69	23	72	4	1,170	−27	610	7,600	13
	60	21	28	2	1,000	−30	670	9,000	11
	23	38	162	6	1,910	−12	700	10,800	28
	18	43	164	7.2	1,460	−7	700	11,000	33
Polyvinyl acetate	100	40	47	1.0	1,900	−10	330	5,500	
	96.5	40	60	6.0	1,000	−10	400	4,000	
	58.5	43	70	3.3	1,500	−7	300	4,000	
	45.5	45	210	5.0	1,480	−5	500	6,000	
Polyvinyl propionate	98.5	8	104	10	600	−42	300	4,000	
	72.6	8	240	17	700	−42	380	4,000	
	53.4	21	263	12	1,000	−29	460	4,700	
	34.7	33	287	23	800	−17	420	8,000	
Polyvinyl butyrate	76	6	80	6	750	−44	180	2,000	
	67	9	170	17	640	−39	360	5,000	
	30	40	400	20	700	−17	700	8,400	
Polyvinyl isobutyrate	96.7	25	81	4.4	1,000	−25	300	5,000	
	77.0	25	88	4.3	910	−25	340	4,000	
	56.0	31	114	5.0	1,000	−19	350	3,000	
	34.7	35	300	10.0	800	−15	660	9,000	
Polyvinyl alcohol		95	1000	200	1,500	+45	700	5,000	

TABLE 6

Comparison of Values of the Vitrification Temperature Determined by Two Methods

Polyvinyl formate			Polyvinyl acetate		
Content of ester groups (mole-%)	Vitrification temperature		Content of ester groups (mole-%)	Vitrification temperature	
	In the Marei apparatus	In the dilatometer		In the Marei apparatus	In the dilatometer
99.8	28	30	100	30	30
78.0	19	17	88	30	30
36.0	7	9	70	28	30

TABLE 7

Interaction Energies for Hydrocarbon Groups in Fatty Acids

Group	Interaction Energy
$CH_3 \cdot CH_2 -$	2,770
$CH_3 \cdot CH_2 - CH_2 -$	3,760
CH_3 CH_3 > $CH -$	4,500

When polyvinyl alcohol is esterified with acetic acid, the hydrogen bonds disappear, and weaker Van der Waals forces appear. Also, the interactions of the main-chain carbon atoms are weakened, since the ester groups are larger than the hydroxyls and move the chains apart. Owing to the change in the character of the intermolecular forces, the molecular interactions of the polyvinyl acetate chains are reduced to 3200 kcal, and T_v is greatly lowered. When the acetyls are replaced by propionyls, the character of

the intermolecular forces does not change. In themselves, the hydrocarbon groups of the propionyls show higher cohesion forces than the acetyls, so that T_v should not fall, but the increased separation of the chains greatly reduces the Van der Waals forces acting between the main-chain carbons, and this has a deciding effect on the value of the molecular interaction. The vitrification temperature of polyvinyl propionate is 32° lower than that of polyvinyl acetate.

Further separation of the chains, when considered in its relation to the character of the Van der Waals forces, should have less effect on the reduction of the interaction between chains, and therefore, the difference between polyvinyl butyrate and polyvinyl propionate in molecular interaction should be less than that between the propionate and the acetate. It is in fact found that the vitrification temperature of polyvinyl butyrate is close to that of polyvinyl propionate.

Introduction of an isoalkanoyl group increases the interaction between the chains, although such groups will screen the main chain considerably more strongly than groups of normal structure. This is confirmed by calculations, based on available data [7], of the interaction energies for the hydrocarbon groups of fatty acids (Table 7).

The cohesion forces of the isobutryl group are greater than those of the propionyl and butyryl groups, and the vitrification temperature of polyvinyl isobutyrate is therefore higher than the vitrification temperatures of the propionic and butyric esters. The fact that the vitrification temperatures of polyvinyl formate and polyvinyl acetate are identical is not altogether understandable, when only the dependence of T_v on molecular interaction forces is considered. There are indications, however, that the vitrification temperature will depend also on the heights of the potential barriers in the molecule which hinder the rotation of the chain units [8].

The higher the potential barrier in a polymer molecule, the higher the vitrification temperature. The height of the potential barrier in a polymer depends on the rigidity of the chain and, in particular on the kind of side groups present. In polyvinyl acetate the chains are farther apart than in polyvinyl formate, but movement of the units of the chain is more greatly hindered in the first polymer than in the second, since the acetate side groups are heavier than the formate groups and are bound to create a higher potential barrier. The effect of the separation of the chains by the acetate groups is neutralized by the hightening of the potential barrier.

In polyvinyl acetate, the main effect on the vitrification temperature is associated with the rigidity of the chain, i.e. the quantitative change in the potential barrier as we pass from polyvinyl formate to polyvinyl acetate has a qualitative effect on the properties of the latter. It must be supposed that in esters of homologs of acetic acid, the main effect is to be associated with the separation of the chains, and quantitative changes in the potential barriers do not result in a sudden jump and qualitative change in the properties of the polymers.

It will be seen from Fig. 1 that the introduction of up to 20-30 mole-% of hydroxyl groups in the polyesters has practically no effect on the vitrification temperatures of the polyesters. When the hydroxyl content is increased further, T_v rises which may be explained by increased molecular interaction, due to the formation of strong hydrogen bonds between hydroxyls of neighboring chains.

Polyvinyl formate is exceptional. The introduction of 35 mole-% of formyl groups into polyvinyl alcohol lowers the vitrification temperature to a much greater extent than the introduction of the same proportion of the other acyl groups that we have investigated. When more than 60 mole-% of formyl groups are introduced, the vitrification temperature begins to rise. Hence, within the range 35-60 mole-% of formyl groups, there is a minimum on the curve for the dependence of the vitrification temperature on the content of ester groups. As already pointed out, the position of the minimum does not depend on the method of determining the vitrification temperature. The presence of the minimum indicates that at a formyl content of 35-55 mole-% the interaction between the chains is greatly reduced, in spite of the fact that 65-45 mole-% of free hydroxyl groups are present and that these hydroxyl groups would be expected to form hydrogen bonds between the chains, as in other esters. We consider that in the formic esters the free hydroxyls must form hydrogen bonds within the chain itself and not between the chains.

The structures of the chains of polyvinyl acetate and polyvinyl alcohol are known [9]. The diagrams in Fig. 2 show the structures of polyvinyl acetate and polyvinyl formate chains containing hydroxyl groups as well as ester groups, and they indicate that in polyvinyl formates internal hydrogen-bonding can indeed occur.

It will be seen from Fig. 2 that in both molecules the distance between the oxygen at the double bond and the hydrogen of the neighboring hydroxyl is the same (2.4 Å). In polyvinyl acetate, however, the formation of a hydrogen bond is sterically hindered by a carbon-carbon bond, and this hindrance is not present in polyvinyl formate. Hence, when the formyl content is 50 mole-% and each hydroxyl hydrogen can be paired with an oxygen, internal hydrogen bonds will probably be formed. When the content of hydroxyl groups is higher than 50-60 mole-%, part of them will remain free and hydrogen bonds may be formed between the chains; the vitrification temperature then

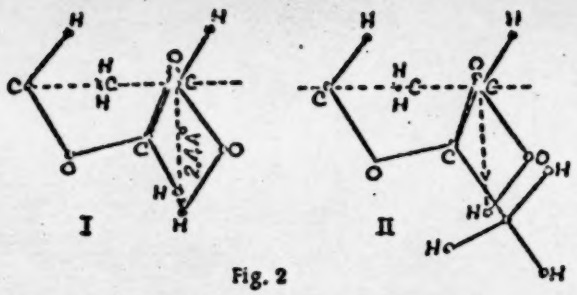

Fig. 2

rises. The vitrification temperature rises also when the formyl content rise above 60 mole-%. The replacement of hydroxyls by formic ester groups then results in increased interaction between the chains, probably as a result of the interaction of the formic ester groups themselves.

As already indicated, the mean length of the main chains was almost the same for all of the esters obtained. This made it possible for a comparison to be made of the mechanical properties of the polymers. The mechanical tests were carried out on films at various temperatures, but under conditions identical with respect to the states of the polymers: for the highly elastic state at a temperature 10° higher than T_v and for the vitreous state at a temperature 40° lower than T_v.

The results (Table 5) show that, for the highly elastic state, as the number of free hydroxyls increases, the strengths of all of the esters, apart from polyvinyl formate, also increase. It is of practical importance that the presence of up to 20-30 mole-% of hydroxyl groups, while not raising the vitrification temperature, increases the strengths of the esters. It is very important also that a considerable increase in strength is not accompanied by any appreciable change in the extension at break. For the highly elastic state, the lowest strengths (60-200 kg/sq.cm) and greatest elongations at break (2000-1500%) are given by polyvinyl acetates and formates. For the series of polyvinyl formates, the lowest strength (28 kg/sq.cm) and lowest extension (1000%) is found for polymers having a formyl content of about 60 mole-%. It may be considered that this anomaly, as also the existence of a minimum vitrification temperature for this ester, is to be associated with the formation of internal hydrogen bonds. The propionic, butyric, and isobutyric esters are approximately equal in strength (80-100 kg/sq.cm) and in extension at break (600-1000%).

The elastic modulus is low for all of the polymers in the highly elastic state (1-20 kg sq.cm). It is particularly low for polyvinyl formates (apart from those having a hydroxyl content of 80 mole-%) and polyvinyl acetates (1-5 kg/sq.cm), indicating that the interaction between chains is very weak. The polyvinyl formates, although having the lowest moduli and strengths in the highly elastic state, have the highest strengths (400-700 kg/sq.cm) and moduli (700-11,000 kg/sq.cm) in the vitreous state. The other esters are very similar to one another with respect to their strength and moduli of elasticity; the values of these properties increase as the content of free hydroxyls increases.

SUMMARY

1. For the first time the vitrification temperatures have been determined and the mechanical properties have been characterized for the full esters formed by polyvinyl alcohol with formic, propionic, butyric, and isobutyric acids, for some of the partial-hydrolysis products of these esters, and for partial acetic esters of polyvinyl alcohol.

2. It has been established that the vitrification temperatures of the investigated polyvinyl esters (except polyvinyl formate) remain constant until the content of free hydroxyls attains 30 mole-%, and then rise as the content of ester groups falls.

3. The formic esters are exceptional: the vitrification temperature passes through a minimum for a hydroxyl content of about 40-60 mole-%.

4. An explanation has been suggested for the anolmalous variation in the vitrification temperature of the formic esters of polyvinyl alcohol.

5. For al of the investigated polyvinyl esters, apart from the fully substituted butyric ester, determinations have been made of the tensile strength, e astic modulus, and extension at break of films of the polymer in the highly elastic and vitreous states.

6. It has been established that, as the proportion of free hydroxyls in the polymers increases, the tensile strengths and elasticity moduli of films prepared from them also increase. Formic esters are exceptional, since in the highly elastic state there is a minimum strength at a hydroxyl content of 40 mole-%.

7. For films in the highly elastic state, the extension at break varies very little as the proportion of free hydroxyls in the polymer rises from zero to 70 mole-%.

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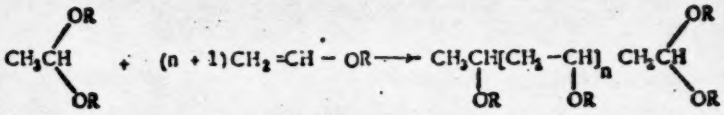
POLYMERIZATION OF VINYL COMPOUNDS.

COMMUNICATION 2. STEPWISE SYNTHESIS OF POLY[ETHYL VINYL ETHER]

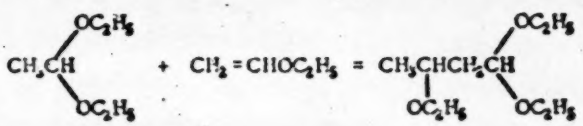
M. F. Shostakovsky and V. A. Gladyshevskaya

Stepwise synthesis is a new way of preparing polymers of low molecular weight. As is well known, a stepwise process proceeds gradually from one stage to another with formation of a series of products of increasing complexity, each of them being a pure individual compound. In a previous investigation [1] we have effected the stepwise synthesis of poly[butyl vinyl ether] according to the scheme:



(n = 0, 1, 2, etc.).

It would be expected that by the use of suitable ethers and acetals of lower boiling point in place of buyl vinyl ether and acetaldehyde dibutyl acetal the isolation of the more complex products would be facilitated, and in the present investigation we have effected the syntheses of some ethoxy compounds. The reactions proceeded according to the following schemes:



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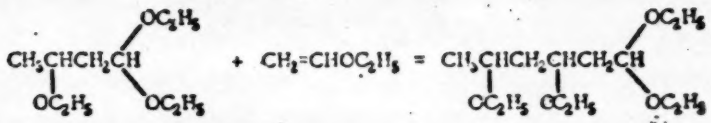

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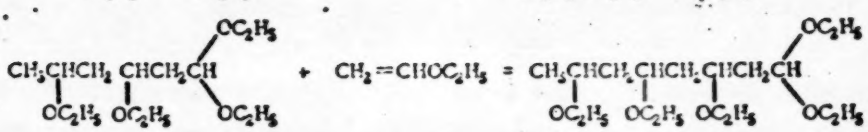

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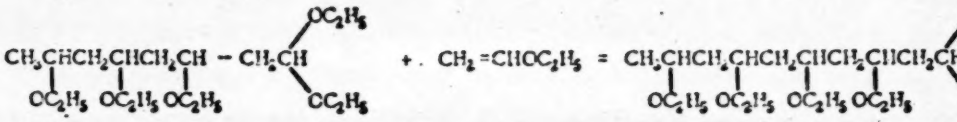

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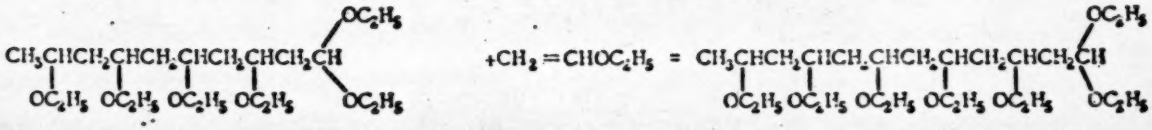


(5)

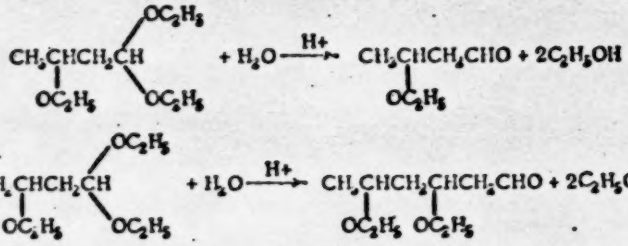
In carrying out these syntheses we were guided by the regularities that we had observed in our work on the butoxy compounds [1]. Examples of the reaction of acetals with α, β-unsaturated ethers have appeared in the literature: in a patent [2], Mueller-Gumadi and Piereh have described the reactions of acetaldehyde acetals with vinyl ethers in presence of catalysts that promote the polymerization of vinyl ethers, and in a paper by Hoaglin and Hirsh [3] this reaction has been studied for a fairly large number of acetals and α, β-unsaturated ethers.

As a result of our experiments we have synthesized a series of ethoxy compounds – from the dimer to the hexamer inclusive. It is to be expected that stepwise synthesis will not stop short at this point, and in fact, after separation of the hexamer, the reaction mixture still contained products higher in molecular weight than the hexamer. It was not found possible, however, to isolate these products in the pure state, since they decomposed when distilled.

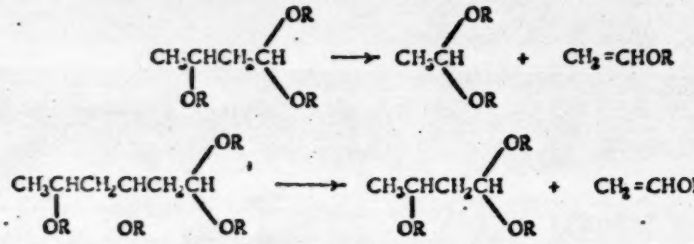
We have determined various constants for our products, and these are found to vary in a regular manner. Among the constants of these synthetic low-molecular-weight products, the viscosity is of special interest.

As is well known [4, 5], the viscosity of a macromolecular compound is of great importance for the determination of its molecular weight. From the relation found between molecular weight and viscosity, the constant K is calculated, and the accuracy with which this constant can be calculated is largely dependent on the care with which the macromolecular compound is fractionated. Hence, the alkoxy compounds that we have isolated, being individual low-molecular-weight products of the polmerization of vinyl ethers, can be used in the determination of the value of K characteristic of this class of polymers.

The ethoxy compounds that we have prepared were subjected to hydrolysis in order to prove the presence of terminal acetal groups:



The aldehyde resulting from the hydrolysis was determined quantitatively by the bisulfite method [6], and it was found that the conditions required for the hydrolysis varied for the different polyethoxy compounds. The higher the molecular weight of the ethoxy compound, the milder the conditions required for its hydrolysis. The lower members of the series (tri- and tetra-ethoxy) were hydrolyzed by 2% sulfuric acid at room temperature. For the hydrolysis of the products for which n = 2, 3, and 4, sodium bisulfite alone was sufficient, and when acid was used the hydrolysis conditions were too severe and the result for the amount of aldehyde formed was too high. The course of the hydrolysis was greatly dependent also on the concentration of the alkoxy compound and the duration of the experiment. The rate of hydrolysis increased with increase in the degree of polymerization of the ethoxy compound. We have established the same regularities for the polybutoxy compounds [1]. The phenomenon described above can be explained on the assumption that, under hydrolysis conditions, the polyalkoxy compounds are decomposed according to the scheme:



The alkyl vinyl ether formed in this way is itself readily hydrolyzed [6], and the amount of determinable aldehyde is therefore increased. We observed decomposition of this sort when we subjected our synthesized polyalkoxy compounds to repeated fractional distillation with a view to their purification. Polymers of higher molecular weight were also highly unstable under these conditions. Owing to the presence of side reactions under the conditions required in the hydrolysis of the polyalkoxy compounds, such hydrolysis cannot be recommended at present as a method of quantitative analysis.

EXPERIMENTAL

1. Synthesis of 1,1,3-Triethoxybutane (I). The starting materials for the synthesis were: acetaldehyde diethyl acetal, prepared by the condensation of ethyl vinyl ether with ethanol [7]; b.p. 103-104° (760 mm); d_4^{20} 0.8250; n_D^{20} 1.3824; and ethyl vinyl ether, prepared by the method of Favorsky and Shostakovsky [8]; b.p. 35-36° (760 mm); d_4^{20} 0.7535; n_D^{20} 1.3780. A 5% solution of ferric chloride in butyl alcohol was used as catalyst.

To 118 g (1 mole) of the diethyl acetal, 2 g of a 5% solution of ferric chloride in butyl alcohol was added. The mixture was heated to 45° and stirred while addition was made of 36 g (0.5 mole) of ethyl vinyl ether, the rate of addition being regulated so that the temperature remained in the range 45-50°. The experiment was continued for one hour after addition of the ether was complete. The catalyst was then precipitated by addition of 2 g of powdered anhydrous sodium carbonate. The mixture was stirred for three hours, and then filtered. The colorless liquid ob-

tained (144 g) was vacuum-distilled, and yielded:

Fraction I, b.p. 36-38° (15 mm);	35.6 g
Fraction II b.p. 38-70° (10 mm);	1.2 g
Fraction III b.p. 59-60° (3 mm);	53.2 g
Fraction IV b.p. 61-104° (3 mm);	0.9 g
Fraction V b.p. 104-105° (3 mm);	32.4g
Fraction VI b.p. 106-138° (3 mm);	0.7 g
Fraction VII b.p. 138-139° (3 mm);	14.3 g
Residue	4.2 g

As a result of repeated fractionations, Fraction I yielded unchanged acetaldehyde diethyl acetal, b.p. 104°, d_4^{20} 0.8250; n_D^{20} 1.3824; and Fraction III yielded 1,1,3-triethoxybutane (I), b.p. 60° (3 mm); d_4^{20} 0.8743; n_D^{20} 1.4073; Found MR 53.53; for $C_{10}H_{22}O_3$ Calculated MR 53.31; Calculated M 190; found M 190; 187; viscosity 1.273 centipoise. Literature data [3]: b.p. 68° (10 mm); $d_{15.6}^{20}$ 0.878; n_D^{20} 1.4069.

	Found %:	C 63.02; 62.87; H 11.91; 11.70
$C_{10}H_{22}O_3$	Calculated %:	C 63.11; H 11.65

Fraction V yielded 1,1,3,5-tetraethoxyhexane (II), b.p. 104° (3mm); d_4^{20} 0.9010; n_D^{20} 1.4202; Found MR 73.61; for $C_{14}H_{30}O_4$ calculated MR 73.42; found M 255; 252; calculated M 262. The literature [3] gives b.p. 107° (5 mm) $d_{15.6}^{20}$ 0.902; n_D^{20} 1.4200.

Fraction VII yielded 1,1,3,5,7-pentaethoxyoctane (III), b.p. 136-138° (3 mm); d_4^{20} 0.9160; n_D^{20} 1.4280; found MR 93.80; for $C_{18}H_{38}O_5$ calculated MR 93.54; found M 325; 328; calculated M 334. The literature [3] gives b.p. 110-116° (0.5 mm); $d_{15.6}^{20}$ 0.917; n_D^{20} 1.4281.

The intermediate fractions (II, IV, and VI) were not investigated because of their very small amounts.

2. Synthesis of 1,1,3,5-Tetraethoxyhexane (II). The reactants were 95 g (0.5 mole) of 1,1,3-triethoxybutane, b.p. 60-61° (3 mm), d_4^{20} 0.8739; n_D^{20} 1.4070 , and 18 g (0.25 mole) of ethyl vinyl ether. The reaction conditions were the same as those of Experiment 1. The product was 108 g of a slightly colored liquid, which was vacuum-distilled.

As a result of numerous fractionations the following compounds were isolated: a) unchanged 1,1,3-triethoxybutane (43.7 g), b.p. 60-62° (3 mm), d_4^{20} 0.8740; n_D^{20} 1.4068; b) 1,1,3,5-tetraethoxyhexane (II) (28.4 g), b.p. 103-104°; d_4^{20} 0.9004; n_D^{20} 1.4200; found MR 73.63; for $C_{14}H_{30}O_4$ calculated MR 73.42; found M 256, 254; calculated M 262; viscosity 3.253 centipoise (see Experiment 1, Fraction VI);

	Found %:	C 64.03; 64.21; H 11.63; 11.21
$C_{14}H_{30}O_4$.	Calculated %:	C 64.08; H 11.50

c) 1,1,3,5,7-pentaethoxyoctane (III) (10.3 g), b.p. 137-139° (3 mm); d_4^{20} 0.9170; n_D^{20} 1.4280; found MR 93.70; for $C_{18}H_{38}O_5$ calculated MR 93.54; found M 324; 320; calculated M 334 (see Experiment 1, Fraction VII); d) 1,1,3,5,7,9-hexaethoxydecane (IV) (8.4 g), b.p. 168-170° (3 mm); d_4^{20} 0.9338; n_D^{20} 1.4360; found MR 113.68 for $C_{22}H_{46}O_6$; calculated MR 113.65; found M 399; 395; calculated M 406; viscosity 17.846 centipoise.

	Found %:	C 64.60; 64.40; H 11.25; 11.46
$C_{22}H_{46}O_6$.	Calculated %:	C 64.98; H 11.40

In this synthesis we prepared the compound for the first time.

3. Synthesis of 1,1,3,5,7-Pentaethoxyoctane (III). The reactants were 132 g (0.5 mole) of 1,1,3,5-tetraethoxyhexane, b.p. 103-104° (3 mm), d_4^{20} 0.9004; n_D^{20} 1.4200, and 24 g (0.33 mole) of ethyl vinyl ether. The reaction conditions were the same as those of Experiment 1. The product was 142 g of a slightly colored liquid, which was distilled repeatedly under reduced pressure. Apart from unchanged 1,1,3,5-tetraethoxyhexane (65.4 g), the following products were obtained: a) 1,1,3,5,7-pentaethoxyoctane (III) (27.3 g), b.p. 137-139° (3 mm); d_4^{20} 0.9166; n_D^{20} 1.4283; found MR 93.81; for $C_{18}H_{38}O_5$ calculated MR 93.54; found M 330; 326; calculated M 334; viscosity 7.650 centipoise [see Experiment 1, Fraction VII and Experiment 2, compound (c)].

	Found %:	C 64.48; 64.24; H 11.27; 11.36
$C_{18}H_{38}O_5$.	Calculated %:	C 64.63 H 11.45

b) 1,1,3,5,7,9-hexaethoxydecane (IV) (15.6 g) b.p. 168-170° (3 mm) ; d_4^{20} 0.9340; n_D^{20} 1.4365; found MR 113.77; for $C_{22}H_{46}O_6$ calculated MR 113.65; found M 392; 389; calculated M 406 (see Experiment 2, compound (d)).

e) 1,1,3,5,7,9,11-heptaethoxydodecane (V) (12.3 g; b.p. 190-192° (3 mm); d_4^{20} 0.9107; n_D^{20} 1.4390; found MR 133.65; for $C_{26}H_{54}O_7$ calculated MR 133.77; found M 488, 483; calculated M 478.

	Found %:	C 65.48;	65.26;	H 11.30; 11.09
$C_{26}H_{54}O_7$.	Calculated %:	C 65.23;		H 11.37

In this synthesis we prepared the compound for the first time.

4 Hydrolysis of the Ethoxy Compounds. a) The hydrolysis of 1,1,3-triethoxybutane and 1,1,3,5-tetraethoxyhexane was carried out in a flask containing 10 ml of 2% sulfuric acid and 20 ml of 0.2 N sodium bisulfite, the weighed amount of substance (0.025-0.150 g) being added in a small sealed tube, which was broken by shaking the flask vigorously. Excess of bisulfite was titrated with 0.1 N iodine – after 60 minutes for 1,1,3-triethoxybutane, and after 30 minutes for 1,1,3,5-tetraethoxyhexane. b) The hydrolysis of the penta-, hexa-, and hepta-ethoxy compounds was carried out in absence of sulfuric acid, 20 ml of 0.2 N sodium bisulfite being added as before. The conditions were the same in other respects. Excess of bisulfite was titrated after two hours for 1,1,3,5,7-pentaethoxyoctane, and after 30 minutes for 1,1,3,5,7,9-hexaethoxydecane; for 1,1,3,5,7,9,11-heptaethoxydodecane, the titration was performed immediately after addition of the substance to the bisulfite solution.

TABLE

Hydrolysis of Ethoxy Compounds

Ethoxy compound	Extent of hydrolysis of ethoxy compound (%)
1,1,3-Triethoxybutane	95.9 96.3
1,1,3,5-Tetraethoxyhexane	96.5 96.7
1,1,3,5,7-Pentaethoxyoctane	96.8 98.1
1,1,3,5,7,9-Hexaethoxydecane	96.9 97.0
1,1,3,5,7,9,11-Hepraethoxydodecane	97.1 97.8

In each case a parallel control experiment was carried out. The degree of hydrolysis was calculated by the formula derived previously [6]. The results of the hydrolysis of the ethoxy compounds are given in the table.

SUMMARY

1. The stepwise synthesis of pure individual members of the poly[ethyl vinyl ether] series has been effected.

2. The following substances have been isolated and characterized: 1,1,3-triethoxybutane, 1,1,3,5-tetraethoxyhexane, 1,1,3,5,7-pentaethoxyoctane; 1,1,3,5,7,9-hexaethoxydecane, and 1,1,3,5,7,8,11-heptaethoxydodecane.

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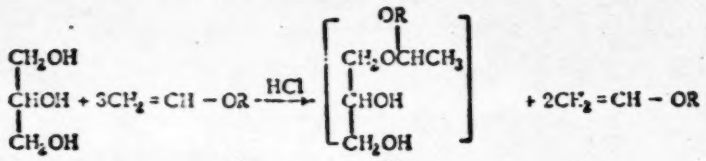
REACTIONS BETWEEN VINYL COMPOUNDS AND MULTIFUNCTIONAL COMPOUNDS

COMMUNICATION 4. REACTION OF ALKYL VINYL ETHERS WITH GLYCEROL AND WITH GLYCEROL 1,2- AND 1,3-CYCLIC ACETALS

M. F. Shostakovsky, V. V. Zhebrovsky, and M. A. Medelyanovskaya

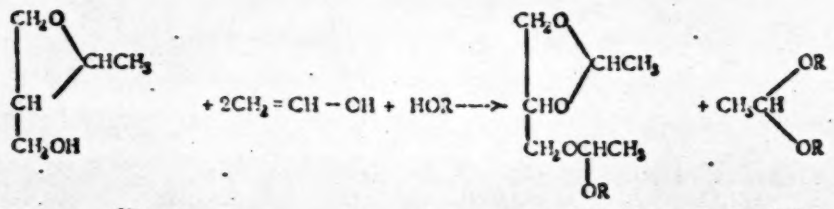
The present paper describes a study of the reaction of alkyl vinyl ethers with glycerol and with glycerol 1,2- and 1,2-cyclic acetals (1,2- and 1,3-O-ethylideneglycerols) in presence of traces of hydrochloric acid; the work forms an extension of our investigations on the synthesis of cyclic acetals of glycerol and of derivatives of these. We have already shown [1] that reaction of equimolecular proportions of ethyl vinyl ether and glycerol yields a mixture consisting mainly of 1,2- and 1,3-O-ethylideneglycerols, and that the same reaction with butyl vinyl ether yields 1,2-O-ethylideneglycerol as the main product. In the present investigation we have established that reaction of alkyl vinyl ethers with glycerol in the molar ratio of 3:1 yields, in addition to other acetals, mixed acetals of glycerol and monohydric alcohols. Thus, the concentrations of the reactants have a considerable effect on the course of the acetal-formation reaction, and by varying them we may direct the synthesis in the desired direction.

When ethyl vinyl ether or butyl vinyl ether reacts with glycerol in the proportions indicated above, it is clear that, in the first place, the corresponding mixed acetal of glycerol and the monohydric alcohol (I) must be formed:



(I)

The mixed acetal of glycerol (I) will then undergo a change leading to the formation of 1,2-O-ethylideneglycerol (II), with elimination of the free alcohol. The cyclic acetal (II) will react with the alkyl vinyl ether and form the complex acetal of glycerol (III), and at the same time the free monohydric alcohol will react with the alkyl vinyl ether with formation of the corresponding acetal (IV):

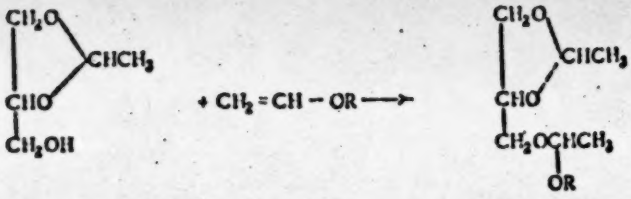


(II) (III) (IV)

(R is C_2H_5 or C_4H_9).

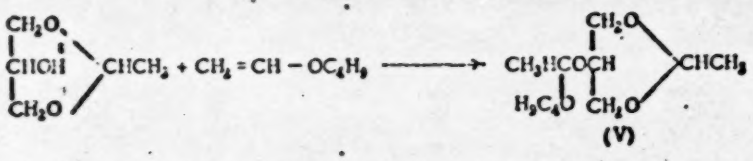
Under these conditions, however, the formation of an acetal of glycerol in which all three hydroxyls would be replaced by alkoxyethoxy groups is excluded, since the cyclization reaction occurring after the formation of the acetal (I) is more rapid than the addition of the alkyl vinyl ether to the other hydroxyls of glycerol.

In order to verify our suggested mechanism of the reaction leading to the formation of the acetals (III) when glycerol is treated with alkyl vinyl ethers, we attempted to synthesize these acetals from alkyl vinyl ethers and the 1,2- and 1,3-O-ethylideneglycerols described previously [2]. An investigation of the products formed by the addition of ethyl vinyl and butyl vinyl ethers to 1,2-O-ethylideneglycerol gave us every reason to suppose that the formation of the acetal (III) did indeed occur according to the scheme:



(R = C_2H_5 or C_4H_9).

In this reaction we isolated 3-O-(1-ethoxyethyl)-1,2-O-ethylideneglycerol and 3-O-(1-butoxyethyl)-1,2-O-ethylideneglycerol. We found also acetals of the corresponding monohydric alcohols, formed as by-products, evidently as a result of the disproportionation of the acetal (III). When butyl vinyl ether reacted with 1,3-O-ethylideneglycerol, the acetal (V) was formed:



(V)

In order to prove the structures of the acetals obtained, they were hydrolyzed, and the hydrolysis products were characterized.

EXPERIMENTAL

The starting materials were: ethyl vinyl ether, b.p. 35-36°, n_D^{20} 1.3782; d_4^{20} 0.7533; butyl vinyl ether, b.p. 93-94°, n_D^{20} 1.4030; d_4^{20} 0.7795; glycerol, b.p. 161-172° (8-14 mm), n_D^{20} 1.4728; d_4^{20} 1.2582; 1,2-O-ethylideneglycerol, b.p. 70-72° (5 mm), n_D^{20} 1.4435; d_4^{20} 1.1232; 1,3-O-ethylideneglycerol, b.p. 60-60.5° (8 mm), n_D^{20} 1.4519; d_4^{20} 1.1422.

The syntheses were carried out in a three-necked flask fitted with mercury-sealed stirrer, thermometer, and reflux condenser.

Reaction of Ethyl Vinyl Ether with Glycerol at a Molar Ratio of 3:1. The reaction mixture consisted of 18.4 g (0.2 mole) of glycerol, 43.2 (0.6 mole) of ethyl vinylether, and 6 drops (0.08 g) of hydrochloric acid. A rise in temperature up to 101° was observed after 60 minutes. After being neutralized with potassium carbonate, the reaction product was fractionally distilled, and yielded:

Fraction I	B.p. 84-95°; 27.7 g;	n_D^{20} 1.3835
Fraction II	B.p. 74-86° (4 mm); 20.18 g;	n_D^{20} 1.4280
Fraction III	B.p. 89-104° (4 mm); 2.3 g;	n_D^{20} 1.4315
Fraction IV	B.p. 149-156° (4 mm); 6.6 g;	n_D^{20} 1.4492

Fraction I had the characteristic odor of acetaldehyde diethyl acetal, and it reacted with sodium, i.e. consisted of a mixture of the diethyl acetal and ethanol. The value found for the acetal content was 93.25; 93.29%.

Fraction II was washed with water and distilled. Its constants [b.p. 86-87° (7 mm); d_4^{20} 1.0088; n_D^{20} 1.4255; found MR 48.26; calculated for $C_9H_{18}O_4$ MR 48.134] corresponded to 3-O-(1-ethoxyethyl)-1,2-O-ethylideneglycerol. Acetal content 98.61; 98.41%. Yield of acetal 9.2 g (23.9%).

	Found %:	C 56.20; 56.26; H 9.54; 9.63
$C_9H_{18}O_4$:	Calculated %:	C 56.82; H 9.53

Reaction of Butyl Vinyl Ether with Glycerol at a Molar Ratio of 3:1. A mixture of 11.5 g (0.125 mole) of glycerol, 37.5 g (0.375 mole) of butyl vinyl ether, and 3 drops (0.042 g) of hydrochloric acid (catalyst) was heated at 50° for four hours. After being neutralized with potassium carbonate, the reaction product was fractionally distilled, when it yielded:

Fraction I, B.p. 66-90°; 18.0 g
Fraction II, B.p. 104-119°; 12.2 g
Fraction III, Undistilled residue, 18.36 g; n_D^{20} 1.4350

Fraction I was a mixture of acetaldehyde dibutyl acetal and butyl alcohol. Redistillation yielded a product of b.p. 64-68° (5-7 mm) and n_D^{25} 1.4112; and the dibutyl acetal content found for this was 91.69; 92.63%.

Fraction II yielded a substance (7.4 g) having b.p. 105-106° (5 mm); n_D^{20} 1.4312; d_4^{20} 0.9816; found MR 57.59; calculated for $C_{11}H_{22}O_4$ MR 57.37. It was 3-O-(1-butoxyethyl)-1,2-O-ethylidendglycerol, obtained in 27.2% yield.

	Found %:	C 60.46; 60.33; H 10.35; 10.21
$C_{11}H_{22}O_4$.	Calculated %:	C 60.52; H 10.11

Synthesis of 3-O-(1-Ethoxyethyl)-1,2-O-ethylideneglycerol from Ethyl Vinyl Ether and 1,2-O-Ethylideneglycerol. A mixture of 7 g of 1,2-O-ethylideneglycerol and 4.27 g of ethyl vinyl ether was prepared in a flask, and one drop (0.014 g) of hydrochloric acid was added, when the temperature of the reaction mixture rose to 90°. The reaction product was neutralized with potassium carbonate and then fractionally distilled from a Favorsky flask. The amount taken for fractionation was 10.95 g, and the fractions isolated were:

Fraction I, b.p. 68-75° (5 mm); 3.07 g; n_D^{20} 1.4312
Fraction II, b.p. 75-78° (5 mm); 4.34 g n_D^{20} 1.4278
Fraction III, b.p. 78-79° (5 mm); 1.45 g; n_D^{20} 1.4282
Residue 0.3 g

Fractions II and III, after treatment with sodium, yielded 2.3 g of 3-O-(1-ethoxyethyl)-1,2-O-ethylideneglycerol, b.p. 84-86° (7 mm); n_D^{20} 1.4275; d_4^{20} 1.0090; found MR 48.45; calculated for $C_9H_{18}O_4$ MR 48.13; the yield of acetal was 20.4%.

	Found %:	C 56.64; 56.61; H 9.47; 9.48
$C_9H_{18}O_4$.	Calculated %:	C 56.82; H 9.53

Synthesis of 3-O-(1-Butoxyethyl)-1,2-O-ethylideneglycerol from Butyl Vinyl Ether and 1,2-O-Ethylideneglycerol. The reactants were 8.85 g of 1,2-O-ethylideneglycerol, 7.5 g of butyl vinyl ether, and one drop (0.014 g) of hydrochloric acid. When the catalyst was added, there was a rise in temperature to 87°. Fractional distillation of 15.85 g yielded:

Fraction I, b.p. 64-104° (8 mm); 1.02 g; n_D^{20} 1.4262
Fraction II, b.p. 112-114°; 13.4 g; n_D^{20} 1.4318
Residue 1.10 g; n_D^{20} 1.4450

Refractionation of Fraction II yielded 10.50 g of 3-O-(1-butoxyethyl)-1,2-O-ethylideneglycerol, b.p. 115-117° (8-9 mm); d_4^{20} 0.9816; n_D^{20} 1.4312; found MR 57.57; calculated for $C_{11}H_{22}O_4$ MR 57.37. Acetal content 98.20; 98.31%. Yield 66.6%.

	Found %:	C 60.65; 60.68; H 10.15; 10.19
$C_{11}H_{22}O_4$.	Calculated %:	C 60.52; H 10.11

Hydrolysis of 3-O-(1-Butoxyethyl)-1,2-O-ethylideneglycerol. The acetal (5 g) was heated with 20 ml of 2% sulfuric acid in a water bath for one hour. The resulting solution was cooled, saturated with potassium carbonate, and extracted with ether. The residue after removal of ether was 1.1 g (61%) of butyl alcohol, b.p. 115-116° and n_D^{20} 1.4062.

Synthesis of 2-O-(1-Butoxyethyl)-1,3-O-ethylideneglycerol from Butyl Vinyl Ether and 1,3-O-Ethylideneglycerol. Reaction of 4.7 g of 1,3-O-ethylideneglycerol with 3.47 g of butyl vinyl ether in presence of one drop of hydrochloric acid was accompanied by a rise in temperature to 70°. Distillation yielded:

Fraction I, b.p. 63-106° (5 mm); 1.54 g; n_D^{20} 1.4222

Fraction II, b.p. 112-116° (5 mm); 3.9 g; n_D^{20} 1.4401

Residue 1.5 g; n_D^{20} 1.4620

Refractionation of Fraction II yielded 2.70 g of a substance having b.p. 106-107° (3-4 mm); d_4^{20} 1.0025; n_D^{20} 1.4410; found M 217.3; 218.8; calculated for $C_{11}H_{22}O_4$ M 218.28; found MR 57.43; calculated MR 57.37. Acetal content 98.78; 98.31%. The yield of 2-O-(1-butoxyethyl)-1,3-O-ethylideneglycerol was 35.6%.

	Found %:	C 60.30; 60.17; H 10.21; 10.13
$C_{11}H_{22}O_4$.	Calculated %:	C 60.52; H 10.11

SUMMARY

1. The following reactions have been investigated: the interaction of ethyl vinyl ether and of butyl vinyl ether

with glycerol at a molar ratio of 3 : 1; the addition of ethyl vinyl ether and of butyl vinyl ether to 1,2-O-ethylideneglycerol; and the addition of butyl vinyl ether to 1,3-O-ethylideneglycerol.

2. It has been shown, for the first time, that the main products of the reactions of ethyl vinyl and butyl vinyl ethers with glycerol are 3-O-(1-ethoxyethyl)- and 3-O-(1-butoxyethyl)-1,2-O-ethylideneglycerols (III) and acetals of the corresponding monohydric alcohols (IV).

3. By the reaction of 1,2-O-ethylideneglycerol with ethyl vinyl and with butyl vinyl ethers, complex cyclic acetals of glycerol (III) are formed.

4. 2-O-(1-Butoxyethyl)-1,3-O-ethylideneglycerol (V) has been synthesized for the first time from 1,3-O-ethylidene glycerol and butyl vinyl ether.

LITERATURE CITED

[1] M. F. Shostakovsky, V. V. Zhebrovsky, and M. A. Medelyanovskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1954, No. 1, 166. *

[2] M. F. Shostakovsky, V. V. Zhebrovsky, and M. A. Medelyanovskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1954, No. 4, 683. **

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* See Consultants Bureau Translation, p. 137.

** See Consultants Bureau Translation, p. 583.

REACTIONS BETWEEN VINYL COMPOUNDS AND MULTIFUNCTIONAL COMPOUNDS

COMMUNICATION 5. REACTION OF GLYCEROL TRIVINYL ETHER WITH MONOHYDRIC ALCOHOLS

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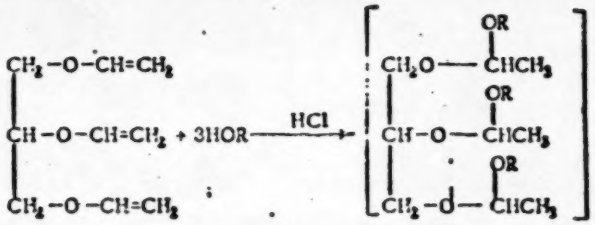
In connection with our study of the chemistry of the formation of acetals from vinyl ethers and polyhydric alcohols, it was considered to be of interest to investigate the reactions of a multifunctional vinyl ether with monohydric alcohols, particularly as we had already studied the reaction of acetal formation from polyhydric alcohols and monovinyl ethers [1,2]. We have already shown [3] that in the reaction of multifunctional vinyl ether (glycerol trivinyl ether) with glycols (ethylene glycol and 1,4-butanediol) the main products are cyclic acetals of the glycols and glycerol.

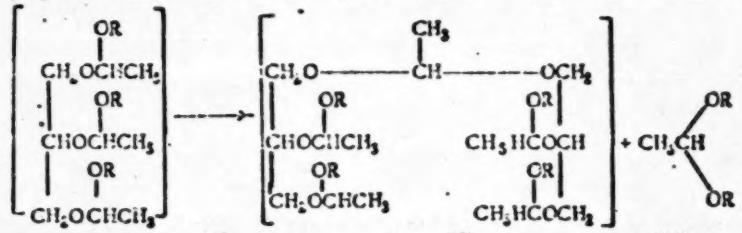
In the present investigation glycerol trivinyl ether has been selected as the multifunctional vinyl ether, and ethyl and butyl alcohols as monohydric alcohols. It appeared possible that interaction between these compounds in presence of traces of hydrochloric acid would lead in the first place to the formation of acetals of glycerol and monohydric alcohols of structure:



(I)

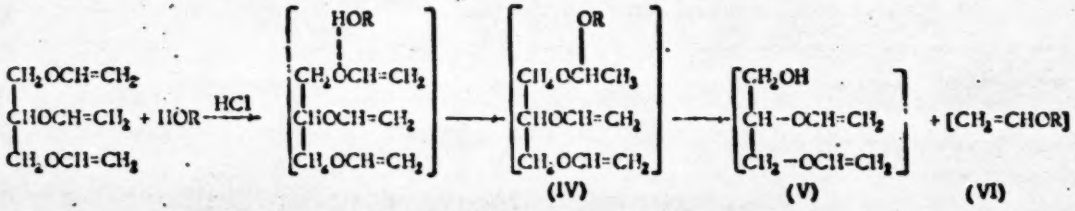
(R = C_2H_5 or C_4H_9) and the corresponding mono- and di-acetals.

Disproportionation of acetals such as (I) could result in the formation of the following compounds:



(II) (III)

Further disproportionation of the acetal (II) could lead to the formation of still more complicated compounds of a similar type. However, an examination of the products formed by the reaction of glycerol trivinyl ether with monohydric alcohols gave reason to suppose that the formation of acetals of glycerol occurred in the following way:

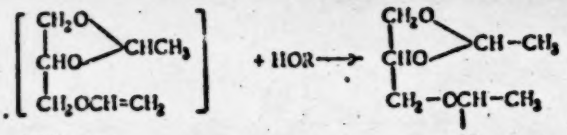


(IV) (V) (VI)

(R = C_2H_5 or C_4H_9).

The first product is the mixed acetal (IV) of glycerol divinyl ether and the monohydric alcohol, and this, being unstable, readily undergoes change with formation of the partial vinyl ether of glycerol (V) and the vinyl ether

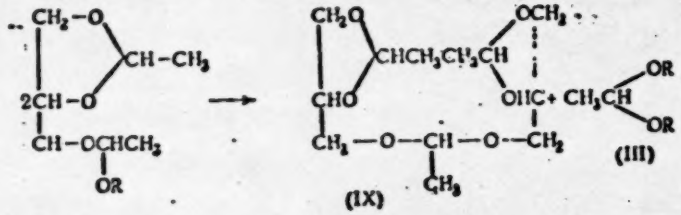
of the monohydric alcohol. The compound (V) then isomerizes to the vinyl acetal (VII), which, reacting further with the monohydric alcohol, yields 3-O-(1-alkoxyethyl)-1,2-O-ethylideneglycerol (VIII):



(VII) (VIII)

By reaction with the alcohol, the vinyl ether of this alcohol (VI), formed by the transetherification reaction, may form the corresponding acetal (III).

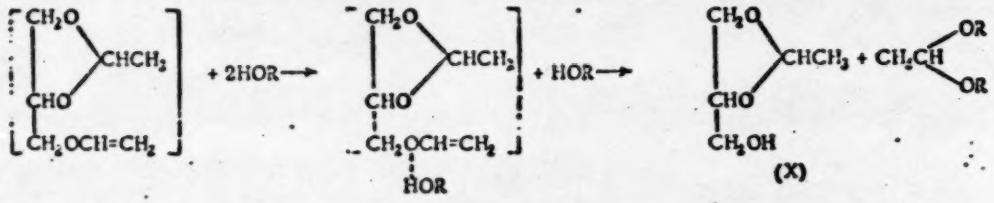
By disproportionation, the complex acetal (VIII) may give:



(IX) (III)

i.e. the diglycerol triacetal (IX) and the acetal of the monohydric alcohol (III).

In addition to the mixed acetal (VIII), 1,2-O-ethylideneglycerol (X) was isolated from the products of the reaction of glycerol trivinyl ether with ethyl and butyl alcohols. It could be formed as follows:



(X)

The acetal (IX) could also be formed by reaction between the acetals (VII) and (X).

We have established that the yields of the cyclic acetals (VIII) and (IX) depend on the proportions of monohydric alcohol and glycerol trivinyl ether. When equimolecular amounts are taken, conditions are favorable for reaction leading to the formation of the intermediate compound (VII). As there is no excess of monohydric alcohol, the free vinyl group of the acetal (VII) remains. The vinyl acetal (VII), reacting with 1,2-O-ethylideneglycerol (X), yields an appreciable amount of the diglycerol triacetal (IX). When the amount of the monohydric alcohol is raised from one molecular proportion to three, for one molecular proportion of glycerol trivinyl ether, experiment shows that the acetal of the monohydric alcohol, the complex acetal of glycerol (VIII), and the diglycerol triacetal (IX) are formed, and the yield of the triacetal (IX) is reduced.

EXPERIMENTAL

The starting substances were glycerol trivinyl ether, b.p. 164-165° and n_D^{20} 1.4385, absolute ethyl alcohol, b.p. 78-78.5° and n_D^{22} 1.3618, and absolute butyl alcohol, b.p. 117-118° and n_D 1.3998.

Reaction of Glycerol Trivinyl Ether with an Equimolecular Proportion of Ethyl Alcohol. A mixture of 42.5 g (0.25 mole) of glycerol trivinyl ether, 11.5 g (0.25 mole) of ethyl alcohol, and 0.028 g of hydrochloric acid was stirred; the temperature rose to 98.5°. Distillation yielded:

Fraction I, b.p. 74-88° (760 mm); 8 g; n_D^{20} 1.3845

Fraction II b.p. 83-95° (7-8 mm); 23.83 g; n_D^{20} 1.4270

Fraction III b.p. 154-157° (7-8 mm); 18.82 g n_D^{20} 1.4478

Residue 1.6 g

Refractionation of Fraction I yielded 7 g of acetaldehyde diethyl acetal, b.p. 98-100°, n_D^{20} 1.3840 (the litera-

ture [4] gives b.p. 103.7-104° and n_D^{20} 1.3820). Analysis by hydrolysis followed by oxime formation gave an acetal content of 104.3; 104.7%. The somewhat high analytical results and the slight departures of the constants from reported values are to be explained by the presence of 3-O-(1-ethoxyethyl)-1,2-O-ethylideneglycerol, the removal of which did not appear to be possible.

Fraction II (15 g) was redistilled twice, and a substance (11.7 g) was isolated which had b.p. 83-84° (6 mm); n_D^{20} 1.4260; d_4^{20} 1.0098; found M 191.0; 189.73; calculated for $C_9H_{18}O_4$ M 190.23; found MR 48.30; calculated MR 48.13 [5]. This substance was 3-O-(1-ethoxyethyl)-1,2-O-ethylideneglycerol (VIII). The acetal content was 98.49; 99.12%.

Fraction II (7 g) was benzoylated, and the benzoic ester of 1,2-O-ethylideneglycerol (1.64 g) was obtained. It had b.p. 147-148° (5 mm) and n_D^{20} 1.5141 [6].

	Found %:	C 64.73; 64.52;	H 6.32; 6.41
$C_{12}H_{14}O_4$.	Calculated %:	C 64.86	H 6.31

Fraction III was redistilled and yielded 16.4 g of a substance that was found to be the acetal derived from three molecules of acetaldehyde and two of glycerol. Its constants were b.p. 153-154° (6 mm), d_4^{20} 1.1072; and n_D^{20} 1.4481, and the literature [7] gives b.p. 160-162° (13 mm), d_4^{24} 1.1067, and n_D^{20} 1.4482. Found M 262.8; 261.7 (cryoscopically in benzene); calcaulated for $C_{12}H_{22}O_6$: M 262.29. Found MR 63.66; Calculated MR 63.074.

Reaction of Glycerol Trivinyl Ether with Ethyl alcohol in the Molar Ratio 1 : 3. A mixture of 42.5 g (0.25 mole) of glycerol trivinyl ether and 34.5 g (0.75 mole) of ethyl alcohol was prepared in a flask, and two drops (0.028 g) of hydrochloric acid were added. The temperature rose to 87°. Fractionation of the reaction product yielded:

Fraction I, b.p. 74-84°; 34.06 g; n_D^{20} 1.3770

Fraction II, b.p. 71-90° (6 mm); 27.1 g; n_D^{20} 1.4350

Fraction III, b.p. 150-155° (6 mm); 13.4 g; n_D^{20} 1.4492

Residue 1.05 g

When redistilled, Fraction I boiled in the same range. It was a mixture of ethyl alcohol and acetaldehyde diethyl acetal. By hydrolysis and oxime formation it was shown that it contained 43.52% (duplicate 43.46%) of the diethyl acetal.

An ethereal solution of Fraction II was washed twice with water. The ether layer was dried with potassium carbonate and distilled, when 10.4 g of 3-O-(1-ethoxyethyl)-1,2-O-ethylideneglycerol (VIII) was obtained. Its constants were: b.p. 86-87° (7 mm); d_4^{20} 1.0090; n_D^{20} 1.4262; found: MR 48.28; calculated for $C_9H_{18}O_4$ MR 48.134. Acetal content 97.71; 98.28%.

Saturation of the wash water with potassium carbonate and extraction with ether yielded 3.6 g of 1,2-O-ethylideneglycerol, having the constants: b.p. 75-77° (8 mm); d_4^{20} 1.1236; n_D^{20} 1.4436; found MR 27.09; calculated for $C_5H_{10}O_3$ MR 27.90. The literature [6] gives b.p. 68-70° (1 mm), d_4^{17} 1.1243; n_D^{17} 1.4415.

After being redistilled, Fraction III boiled at 157-160° (7 mm) and had d_4^{20} 1.1070; n_D^{20} 1.4483. It was the diglycerol triacetal [7].

Reaction of Glycerol Trivinyl Ether with an Equimolecular Proportion of Butyl Alcohol. In the reaction of 34 g (0.2 mole) of glycerol trivinyl ether and 14.82 g (0.2 mole) of butyl alcohol in presence of two drops of hydrochloric acid (0.028 g), a rise in temperature to 83° was observed. Fractional distillation yielded:

Fraction I, b.p. 56-91° (6 mm); 13.26 g; n_D^{20} 1.4250

Fraction II, b.p. 108-110° (6 mm); 25.20 g; n_D^{20} 1.4322

Fraction III, b.p. 149-152° (6 mm); 7.0 g; n_D^{20} 1.4470

Residue 1.6 g

Fraction I, which boiled over a wide range of temperature, was diluted with ether and washed with water. It was not found possible to isolate completely pure acetaldehyde dibutyl acetal from the ether layer, even after repeated distillation. The product isolated (6 g) boiled at 164-165° and had n_D^{20} 1.4150 (the literature [8] gives b.p. 185-186° and n_D^{16} 1.4085). The diacetal content was found to be 87.13; 87.55%. The aqueous layer yielded 0.25 g of 1,2-O-ethylideneglycerol, b.p. 88° (15 mm); n_D^{20} 1.4420 [6].

Redistillation of Fraction II yielded 19.2 g of 3-O-(1-butoxyethyl)-1,2-O-ethylideneglycerol (VIII), the constants of which were b.p. 108-108.5° (6 mm); d_4^{20} 0.9910; n_D^{20} 1.4310; found M 211.9; 219.8; calculated for $C_{11}H_{22}O_4$

M 218.28; found MR 57.17; calculated for $C_{11}H_{22}O_4$ MR 56.95 [5]. The acetal content (by hydrolysis and oxime formation) was 99.79; 99.46%.

Redistillation of Fraction III yielded 5 g of a substance boiling at 151-153° (6 mm) and having n_D^{20} 1.4478. Its constants corresponded to the diglycerol triacetal (IX).

SUMMARY

1. The reactions of glycerol trivinyl ether with ethyl and butyl alcohols have been studied.

2. It has been shown that the main reaction products in the reaction of glycerol trivinyl ether with monohydric (ethyl and butyl) alcohols are the acetaldehyde acetals of the monohydric alcohols, mixed acetals of glycerol and the monohydric alcohol (VIII), and the acetal derived from three molecules of acetaldehyde and two of glycerol (IX).

3. 3-O-(1-Ethoxyethyl)- and 3-O-(1-butoxyethyl)-1,2-O-ethylideneglycerols (VIII) have been isolated and characterized.

4. It has been shown that the reaction of glycerol trivinyl ether with ethyl and butyl alcohols yields the same acetals as those formed by the reaction of ethyl vinyl and butyl vinyl ethers with glycerol.

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*** See Consultants Bureau Translation, p. 583.
**** See Consultants Bureau Translation, p. 313.

MACROMOLECULAR COMPOUNDS. LXXI.

COMMUNICATION 71. POLYCONDENSATION OF 1,2-CHLOROETHANE WITH CHLOROBENZENE IN PRESENCE OF ALUMINUM CHLORIDE

G. S. Kolesnikov, V. V. Korshak, and L. S. Fedorova

Continuing our study [1-3] of polycondensation processes occurring between aliphatic halogen compounds and aromatic hydrocarbons with formation of macromolecular carbon-chain compounds, we have investigated the polycondensation of 1,2-dichloroethane with chlorobenzene in presence of aluminum chloride. The purpose of the investigation was to determine the essential features of the polycondensation reaction between 1,2-dichloroethane and an aromatic hydrocarbon of reduced "functionality", as compared with unsubstituted benzene. The benzene molecule contains six hydrogen atoms that may be replaced with alkyl groups, and the products of the condensation of 1,2-dichloroethane with benzene may therefore have a branched structure, so that three-dimensional condensation products may be formed in which linear molecules of poly[ethylenephenyl] are cross-linked together.

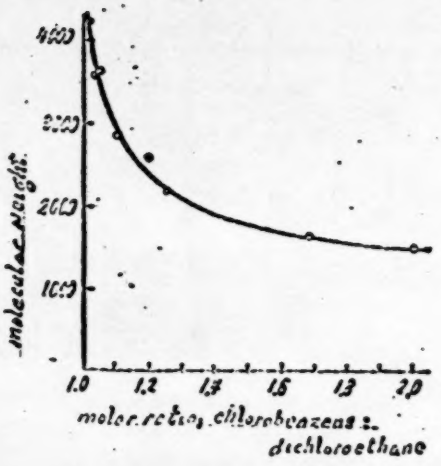


Fig. 1

It is known, however, that the introduction of two substituents into the benzene nucleus renders further alkylation difficult, so that it might be expected that the polycondensation of 1,2-dichloroethane with chlorobenzene would differ somewhat from the polycondensation of 1,2-dichloroethane with benzene, since in the former process a third substituent must enter the benzene nucleus. In order to elucidate the effect of the proportions of the reactants on the properties and yield of reaction products, a series of experiments was carried out in which the duration of the reaction and the amounts of chlorobenzene and aluminum chloride were maintained constant, but the amount of 1,2-dichloroethane was varied. The experimental procedure was the same as that used previously [2], with the exception that, after the solvent had been distilled off, only the symmetrical dichlorobibenzyl was distilled off under reduced pressure. The results are given in Table 1 and in Fig. 1. The molecular weights of the polycondensation products were determined viscosimetrically, K_m being taken as 1.8×10^{-4}.

Table 1 shows that reduction in the excess of chlorobenzene results in increased yield of macromolecular products and reduced yield of the symmetrical dichlorobibenzyl. Also, the molecular weight of the macromolecular polycondensation product, poly[(chloro)ethylenephenyl], rises as the excess of chlorobenzene is reduced, and reaches its highest value when the proportions of the reactants approximate to equimolecular, a fact that is in accord with the theory of linear polycondensation proposed by one of the present authors [4]. It is interesting to note that the formation of three-dimensional condensation products occurs only when the molar ratio of chlorobenzene to 1,2-dichloroethane is unity or less than unity (a 1% excess of chlorobenzene yields a mixture of linear condensation product and three-dimesional polymer), whereas three-dimensional products are formed in the polycondensation of 1,2-dichloroethane with benzene, even when there is a 20% excess of benzene [2]. This indicates that the introduction of a chlorine atom into the benzene nucleus hinders the formation of polycondensation products of branched structure and of the three-dimensional polymers formed from these by reaction among themselves and with linear condensation products.

It may therefore be considered as proved that the functionality of the benzene molecule is reduced by the replacement of a hydrogen by chlorine to a greater extent than would be expected simply on the basis of the reduction of the number of hydrogen atoms in the benzene nucleus. If, in fact the five hydrogens of chlorobenzene and the six hydrogens of benzene are equally prone to replacement by aliphatic connecting bridges, then the reduction of the functionality of benzene from 6 to 5 in chlorobenzene, and to 4 in disubstituted benzenes, should not have any appreciable effect on the tendency of these aromatic hydrocarbons to form branched and three-dimensional structures. However, the introduction of one chlorine atom into the benzene nucleus is sufficient to reduce the tendency to form three-dimen-

sional structures to a very great extent, and the introduction of two substituents into the benzene nucleus has been shown, in an investigation carried out simultaneously with the one now described, to cause the aromatic hydrocarbon to behave as a bifunctional compound, despite the presence of four hydrogen atoms potentially able to be replaced. Hence, the practical, or reactional, functionality of chlorobenzene is less than its potential functionality [5].

TABLE 1

Polycondensation of 1,2-Dichloroethane with Chlorobenzene (Aluminumchloride : chlorobenzene = 0.1)

Molar ratio chlorobenzene : 1,2-dichloroethane	Yield (%) of the symmetrical dichlorobibenzyl	Yield (%) of polymer	Molecular weight of polymer
2.0	21.6	57.9	1570
1.68	15.9	59.3	1720
1.25	8.3	74.1	2230
1.19	7.4	74.7	2580
1.095	5.5	74.8	2850
1.05	3.4	69.1	3640
1.025	3.10	61.3	3590
1.01	—	81.1*	4250**
0.793	—	86.3***	—
0.747	—	76.9***	—

* Including 24.3% of linear polycondensation product and 56.8% of benzene-insoluble three-dimensional polymer.

** Molecular weight of linear polycondensation product.

*** Three-dimensional polymer.

It has already been shown, by two of the present authors and Sinirnova [2,3], that the course of the polycondensation of 1,2-dichloroethane with benzene is determined not only by the proportions of the reactants, but also by the concentration of the catalyst. Since the part played by the catalyst concentration in polycondensation processes has not yet been fully elucidated, we considered it desirable to determine whether the regularities that we observed previously for the condensation of 1,2-dichloroethane with benzene are found also in the reaction of 1,2-dichloroethane with chlorobenzene. With this object in view, we carried out a series of experiments in which the duration of the reaction and the amounts of chlorobenzene and 1,2-dichloroethane remained constant, but the amount of aluminum chloride was varied. The experimental procedure was the same as in the first series of experiments. The results are given in Table 2 and Fig. 2.

TABLE 2

Influence of Catalyst Concentration. Chlorobenzene–dichloroethane = 1.19

Aluminum chloride (moles per 100 moles of 1,2-dichloroethane)	Yield % of the symmetrical dichlorobibenzyl	Yield % of poly[(chloro)ethylenephenyl]	Molecular weight
1.19	0.5	—	
2.38	1.7	68.7	2380
3.57	1.4	67.8	3050
4.74	7.7	70.9	2930
5.94	5.3	63.7	3180
7.14	4.6	72.5	2680
8.32	3.4	74.2	2850
9.56	2.4	82.1	2390
10.71	3.4	73.3	2700

Table 2 and Fig. 2 show that in the polycondensation of chlorobenzene with 1,2-dichloroethane in presence of aluminum chloride, as in the polycondensation of benzene with dichloroethane [3], the concentration of the catalyst is not a matter of indifference. At low aluminum chloride concentrations, no polycondensation products are formed. Increase in the concentration of catalyst results in the formation of macromolecular polycondensation products, and the molecular weight of these products increases with increase in catalyst concentration, but only up to a certain value of this concentration. Further increase in catalyst concentration leads to a reduction in the molecular weight of the poly[(chloro)ethylenephenyl] although the fall is not so marked as in the polycondensation of 1,2-dichloroethane with benzene [3].

Apart from this study of regularities to be observed in the polycondensation of 1,2-dichloroethane with chlorobenzene, we made an investigation of the structure of the products of this reaction. The product of lowest molecular weight to be expected from this reaction is one of the isomeric symmetrical dichlorobibenzyls:

$$2ClC_6H_5 + ClCH_2CH_2Cl \xrightarrow{AlCl_3} ClC_6H_4CH_2CH_2C_6H_4Cl + 2HCl$$

The product of low molecular weight that we obtained boiled at 163-164° (3 mm) after being distilled twice. It was a colorless liquid, which became very viscous when cooled but did not yield any crystals.

In order to determine the structure of this symmetrical dichlorobibenzyl, we subjected it to oxidation and obtained p-chlorobenzoic acid as the sole product. This indicated that the product was essentially 4,4'-dichlorobibenzyl. It is reported in the literature [6] that 4,4'-dichlorobibenzyl does not readily pass into the crystalline state, the trans-

lition never being complete, even after careful distillation and the selection of a narrow fraction.

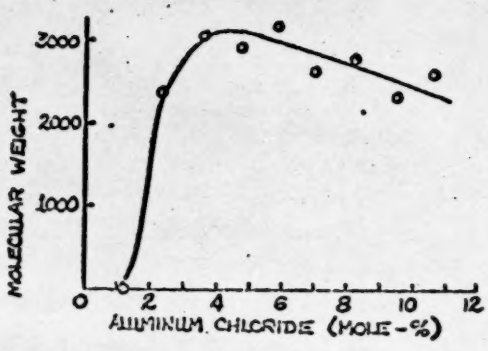


Fig. 2

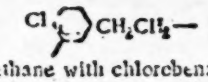
In order to determine the structure of the macromolecular polycondensation products, we submitted them to oxidative degradation, in the hope of obtaining a chlorobenzendicarboxylic acid, the identification of which would indicate the relative positions of the aliphatic bridges —CH_2CH_2— and the chlorine. Analysis of the polycondensation products showed that the composition of the repeating unit was —$C_6H_3ClCH_2CH_2$—.

However, we did not obtain a dicarboxylic acid when we oxidized the polycondensation products with chromic acid mixture. The main product was found to be p-chlorobenzoic acid, which we identified by its melting point, molecular weight (determined by titration with alkali), and elementary composition. After purification, the p-chlorobenzoic acid so obtained melted at 230-235°.

Oxidative degradation with potassium permanganate in acid, neutral, and alkaline media again did not yield a dicarboxylic acid. Hence, by oxidative degradation it was possible to determine the position of only one of the aliphatic connecting bridges with respect to the chlorine atom.

In an attempt to determine the structure of the polycondensation products we examined also their chemical degradation with benzene in presence of aluminum chloride. Two products could be expected as a result of this reaction: 4-chlorobibenzyl (on the basis of the results of oxidative degradation) and an isomeric chlorobibenzyl, the structure of which should indicate the position of the second aliphatic bridge. The products isolated from this degradation reaction were 4-chlorobibenzyl, identified by its melting point, and a very small amount of a liquid, which we did not succeed in identifying.

On the basis of these results we can make some suggestions concerning the structure of these products. It has been proved that the chlorine atom is in the para position to one of the —CH_2CH_2— bridges. From the absence of aromatic dicarboxylic acids in the oxidation products, it may be inferred that the second aliphatic bridge is probably in the position ortho to the chlorine. This supposition is based on the well known fact that the aromatic ring is readily destroyed during the oxidation of aromatic hydrocarbons having a substituent ortho to the aliphatic radical. In the oxidation of such compounds, either the ortho-substituted benzoic acid is not obtained at all, or it is obtained in extremely low yield. Also the orienting effects of the chlorine and the first aliphatic substituent favor the ortho-orientation of the second —CH_2CH_2— bridge. It is well known that in alkylation reactions in presence of aluminum chloride chlorine directs the entering substituent into the ortho and para positions, but an aliphatic residue directs the second aliphatic substituent into the meta position. Since the low-molecular-weight reaction product is 4,4'-dichlorobibenzyl it may be assumed that the first aliphatic residue enters the position para to chlorine, and that the second residue then enters the position ortho to chlorine. It may therefore be assumed that the most probable elementary repeating unit is as follows:



so that the product of the polycondensation of 1,2-dichloroethane with chlorobenzene may be named poly [2-chloro-5-ethylenephenyl].

EXPERIMENTAL

The experimental procedure was the same as that described previously [2], with the exception that only the symmetrical dichlorobibenzyl was distilled off under reduced pressure (over the range 120-130° at 3 mm). The experimental conditions and the results obtained are given in Tables 3 and 4.

Oxidation of Polycondensation Products

Oxidation of the Symmetrical Dichlorobibenzyl. The symmetrical dichlorobibenzyl (10 g) was refluxed with nitric acid (250 ml; sp. gr. 1.1) for 10-11 hours. The mixture was then rendered alkaline with a 20-25% solution of caustic soda, and was boiled for 8-10 hours, during which time 18 g of potassium permanganate was added in 2-g portions. Excess of potassium permanganate was removed by addition of methanol, and the mixture was filtered at the pump. The filtrate was acidified to Congo red, and the precipitated acid was filtered off. After recrystallization from water, the acid melted at 217-218°.

	Found %:	M 145.4; 143.2
$C_7H_5O_2Cl$.	Calculated %:	M 156.6

TABLE 3

Polycondensation of 1,2-Dichloroethane with Chlorobenzene (Chlorobenzene, 112.6 g; aluminum chloride, 13.3 g; time, 4 hours)

Expt. No.	Amount of 1,2-dichloroethane (g)	Amount obtained (g)		Concentration of benzene solution of poly [(chloro)-ethylenephenyl] (g/100 ml)	Specific viscosity	Molecular weight of poly[(chloro)-ethylene-phenyl]
		of the symmetrical dichloro-bibenzyl	of poly [(chloro)-ethylenephenyl]			
1	49.5	27.0	30	1.932	0.0405	1570
2	59.0	23.7	49	3.432	0.0768	1720
3	79.0	16.5	82	3.975	0.115	2230
4	83.2	15.5	87	3.336	0.112	2580
5	90.3	12.5	94.5	3.131	0.116	2850
6	94.3	8.0	91	3.482	0.165	3640
7	95.6	7.5	82	3.506	0.163	3590
8	98.0	–	111•	3.388•••	0.187	4250
9	112.6	–	136••	–	–	–
10	132.5	–	142.5••	–	–	–

• 33.4 g of benzene-soluble polycondensation product and 77.6 g of benzene-insoluble three-dimensional polymer.

•• Three-dimensional polymer.

••• For the soluble polycondensation product.

Analysis of the soluble polycondensation product

	Found %:	C 69.71; 69.66;	H 5.04; .06; Cl 25.51; 25.41
C_2H_3Cl	Calculated %:	C 69.33,	H 5.09; Cl 25.58

TABLE 4

Polycondensation of 1,2-Dichloroethane with Chlorobenzene (Chlorobenzene, 112.6 g; 1,2-dichloroethane, 83.2 g)

Expt. No.	Amount of aluminum chloride (g)	Amount obtained (g)		Concentration of benzene solution of poly [(chloro)ethylene-phenyl] (g in 100 ml)	Specific viscosity	Molecular weight of poly[(chloro)-ethylenephenyl
		of the symmetrical dichlorobibenzyl	of poly[(chloro) ethylenephenyl]			
11	1.33	1.0	–	–	–	–
12	2.65	3.5	79.0	3.312	0.102	2380
13	3.99	3.0	78.0	3.476	0.138	3050
14	5.30	16.0	81.5	3.036	0.116	2930
15	6.65	11.0	73.2	3.833	0.158	3180
16	8.00	9.5	83.4	3.810	0.133	2680
17	9.31	7.0	85.4	3.474	0.142	2850
18	10.70	5.5	94.5	3.047	0.095	2390
19	12.00	7.1	84.3	4.993	0.175	2700

Oxidative Degradation of the Polycondensation Products. A mixture of 20 g of the product of the polycondensation of 1,2-dichloroethane with chlorobenzene, 200 g of potassium dichromate, 600 ml of water, and 150 g of sulfuric acid was boiled for 30 hours. The mixture was then poured into 2-3 times its volume of water, and the precipitate that formed was filtered off. The precipitate was treated with 10% ammonia solution, and the solution was filtered and acidified to Congo red. The precipitated acid was filtered off, washed with a little water, and dried in a vacuum desiccator. During the oxidation a white substance collected in the reflux condenser, and this was found to be identical with the substance isolated from the reaction mixture. After recrystallization from water, the acid melted at 230-235°.

	Found %:	C 53.85; 53.69;	H 3.25; 3.28
C_7H_4OCl	Calculated %:	C 53.69	H 3.22

Degradation of the Polycondensation Products with Benzene

A mixture of 20 g of the product of the polycondensation of 1,2-dichloroethane with chlorobenzene (molecular weight 3150), 20 g of aluminum chloride, and 200 ml of benzene was prepared in a flask fitted with a reflux condenser. The mixture was boiled in a water bath for five hours. Decomposition was then effected with dilute hydrochloric acid, and the usual further treatment was given. Vacuum fractionation yielded 2 g of a fraction boiling over the range 150-200° (3 mm). This fraction solidified, and after recrystallization from alcohol it melted at 49°, which is the melting point of 4-chlorobibenzyl [7].

SUMMARY

1. The polycondensation of 1,2-dichloroethane with chlorobenzene has been studied and the essential features of the process have been established.

2. It has been found that the introduction of a chlorine atom into the benzene nucleus hinders the formation of three-dimensional polycondensation products.

3. The polycondensation product has been investigated, and views have been expressed relating to its structure.

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MACROMOLECULAR COMPOUNDS

COMMUNICATION 72. FORMATION OF A THREE-DIMENSIONAL POLYMER BY REACTION OF POLY[ETHYLENEPHENYL] WITH DIHALOALKANES

V. V. Korshak, G. S. Kolesnikov, and T. A. Soboleva

Investigation of the transarylation reaction of bibenzyl [1], and also of the polycondensation of 1,2-dichloroethane with benzene [2, 3], has shown that at a definite stage of the reaction a three-dimensional product is formed as a result of the cross-linking of the chains of the linear polymer formed in the earlier part of the reaction. An examination of the results obtained has led two of the present authors to suggest that it is mainly the longest molecules that are concerned in the formation of a three-dimensional product in the transarylation of bibenzyl, so that the molecular weight of the poly[ethylenephenyl] remaining in solution is reduced [4].

Since the formation of three-dimensional polymers is of great interest as a process extensively applied in various branches of polymer chemistry, for example, in the vulcanization of rubber and the conversion of resol into resite, we have studied some of the features of this process, as shown in the reactions of poly[ethylenephenyl] with some dihaloalkanes. We have shown previously that the polycondensation of benzene with 1,2-dichloroethane, particularly when the latter is present in excess, results in the formation of three-dimensional products, which are insoluble in benzene and other solvents [2, 3]. It may be expected, therefore, that, by reaction with various dihaloalkanes in presence of aluminum chloride, poly[ethylenephenyl] will yield three-dimensional products as a result of the formation of cross links between linear poly[ethylenephenyl] molecules.

The original poly[ethylenephenyl] used throughout the investigation was an artificially prepared mixture of two samples of separately prepared poly[ethylenephenyl]; they were synthesized and purified in the way already described [2, 3]. The molecular weight, as determined from viscosity measurements on a 3% benzene solution, was 11,470 for the first sample, 2,140 for the second sample, and 5,930 for the mixture.

The following dihaloalkanes were used as cross-linking agents: dibromomethane, 1,2-dibromoethane, 1-bromo-3-chloropropane, 1,4-dibromobutane, and 1,6-dibromohexane. Bromo derivatives were used, rather than chloro derivatives, because their boiling points are higher and the losses during the reaction therefore lower.

The reactions of poly[ethylenephenyl] with these dihaloalkanes were carried out for various concentrations of the latter compounds. The catalyst was anhydrous aluminum chloride (0.9 mole per mole of dihaloalkane). The duration of the reaction and the temperature were the same in all experiments (three hours, 120°). After the reaction the mixture was treated with dilute hydrochloric acid, and then benzene. The insoluble three-dimensional polymer was filtered off and washed with benzene until completely free of benzene-soluble substances. The substance remaining on the filter was the three-dimensional polymer; it was dried and weighed. The soluble poly[ethylenephenyl] was separated from the benzene solution by distilling off the solvent, the residue being dried to constant weight. The results are given in Table 1.

The data in Table 1 show that, when poly[ethylenephenyl] is heated with a dihaloalkane in presence of anhydrous aluminum chloride, an insoluble three-dimensional product is formed in an amount that depends both on the identity of the dihaloalkane and the amount of this taken. The dihaloalkanes can be placed in the following order, corresponding to increasing yield of three-dimensional polymer from a given amount of the dihaloalkane: 1,4-dibromobutane, 1-bromo-3-chloropropane, 1,6-dibromohexane, dibromomethane, and 1,2-dibromoethane.

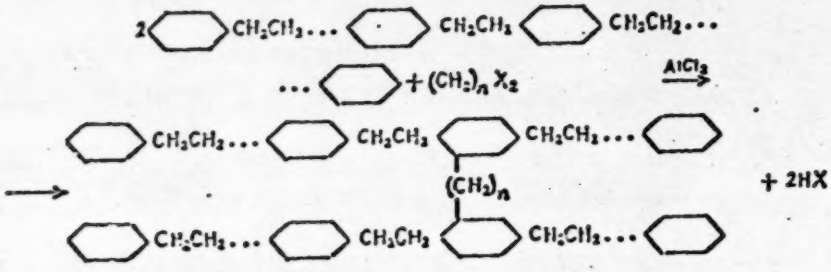
The least active of the cross-linking agents are 1,4-dibromobutane and 1-bromo-3-chloropropane, for they give the lowest yields of three-dimensional polymer. This fact must be associated with the tendency of these halo compounds to form tetrahydronaphthalene and indan derivatives with benzene and its homologs, which leads to a reduction in the amount of the dihalo compound available for cross-linking the poly[ethylenephenyl] and therefore a reduction in the yield of three-dimensional polymer. The remaining investigated dibromo compounds, owing to the operation of stereochemical factors, have no tendency to form rings, and they give higher yields of three-dimensional polymer. The yield of the latter is dependent also on the amount of cross-linking agent, as will be seen from the results given in Table 1. With increase in the amount of cross-linking agent, the yield of three-dimensional polymer rises in a regular manner in all cases.

TABLE 1

Reaction of Poly[ethylenephenyl] with Dihaloalkanes

Dihaloalkane	Amount of dihaloalkane per basic mole of poly[ethylenephenyl] (mole-%)	Amount obtained (% of original amount) of insoluble three-dimensional polymer	Amount obtained (% of original amount) of soluble poly[ethylenephenyl]	Molecular weight of the soluble poly[ethylenephenyl] isolated
Dibromomethane	2.15	16.4	83.4	6290
	6.45	15.3	82.6	5120
	8.60	20.0	80.5	3120
1,2-Dibromoethane	2.15	15.8	76.8	5610
	4.30	24.7	68.0	5700
	8.60	24.0	65.4	5580
	12.90	35.8	61.8	2230
1-Bromo-3-chloropropane	2.15	16.7	81.2	5400
	4.30	18.8	80.0	5170
	12.90	19.8	76.4	3110
1,4-Dibromobutane	2.15	4.9	84.6	6100
	6.45	6.7	79.3	5560
	8.60	9.8	71.4	5150
	12.90	15.6	81.6	4420
1,6-Dibromohexane	2.15	4.0	90.2	5810
	4.30	12.2	81.4	5110
	8.60	16.2	79.1	4670
	12.90	26.4	73.0	4110

The molecular weight of the poly[ethylenephenyl] that does not react is at first almost constant, and only when the amount of cross-linking agent exceeds 8 mole-% is there a noticeable fall in the molecular weight of the soluble polymer. It is clear from this behavior that the cross-linking reaction proceeds in two stages. In the first stage cross-linking occurs between a few (two, three, etc.) linear molecules:

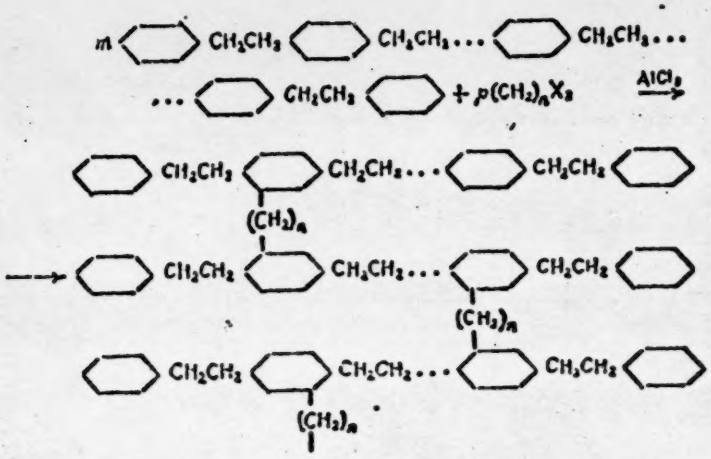


As a result of this, mainly branched molecules arise, and up to a certain degree of complexity they retain their solubility in benzene. The formation of such branched molecules will lead to an increased molecular weight, and this will compensate for the fall in molecular weight due to the higher tendency of the longer poly[ethylenephenyl] molecules to react.

Such branched molecules react further with formation of three-dimensional molecules, and so become insoluble in benzene. This reaction can be represented as follows (see top of following page).

Thus, there is no difference in principle between branched and three-dimensional molecules. The difference lies only in the number of cross links and in the number of linear chains linked together.

As will be readily seen from the results given in Table 1, when the cross-linking agent is present in an amount of greater than 8%, there is a considerable fall in the molecular weight of the soluble poly[ethylenephenyl] that has not reacted. This fall in molecular weight is particularly great in the reaction with 1,2-dibromoethane; it is somewhat less for dibromomethane and 1-bromo-3-chloropropane, and still less for the remaining dibromo compounds. In the reaction with 1,2-dibromoethane, the residual soluble poly[ethylenephenyl] is almost free of the higher-molecular-



weight fraction, and consists almost entirely of the poly[ethylenephenyl] of lower molecular weight which was brought into the reaction as a component part of the original mixture. In this reaction, therefore, the high-molecular-weight component of the original mixture is converted almost completely into three-dimensional polymer. In the reactions with the other dihalo compounds, this feature is not so prominent, but the considerable fall in molecular weight, indicating the greater reactivity of the poly[ethylenephenyl] of higher molecular weight, is again quite obvious.

The original mixture of polymers consisted of ~ 60% low molecular weight (2140) and ~ 40% high molecular weight (11,470) (poly[ethylenephenyl]); whereas the poly[ethylenephenyl] isolated after the reaction with 1,2-dibromoethane in an amount equivalent to 61.8% of the whole of the original mixture had a molecular weight of 2230, that is to say, consisted in effect of the low-molecular-weight component of the original mixture, recovered practically without loss in an almost pure state. This great difference in the reactivities of poly[ethylenephenyl] preparations differing in molecular weight is determined by the variation with molecular weight of the probability of a polymer entering the reaction, as will be readily seen from the following considerations. Let y be the amount of the cross-linking agent (moles per 100 basic moles of polymer), x the degree of polymerization of the polymer, a the number of cross links per polymer macromolecule, and b the number of cross links per repeating unit, then:

$$b = \frac{y}{100}$$

and therefore

$$a = b \cdot x = \frac{y \cdot x}{100}$$

By the use of this equation it is easy to calculate the variation of the number of cross links formed between the macromolecules as a function of the degree of polymerization of the original polymer and of the amount of cross-linking agent, expressed as moles per 100 basic moles of the polymer. The results of this calculation are given in Table 2.

In Fig. 1 the number of cross links per repeating unit of the polymer is shown graphically in its dependence on the degree of polymerization for various amounts of cross-linking agent, expressed as moles per 100 basic moles of polymer. Fig. 1 shows how rapidly the number of cross links falls with increase in the degree of polymerization.

Increase in the amount of cross-linking agent results in a rapid increase in the number of cross links between the macromolecules, as can be readily seen from Fig. 2, which is constructed from the data in Table 2. It is again quite obvious that the magnitude of the molecular weight of the polymer plays an important part, and the number of cross links increases as the molecular weight – or its equivalent, the degree of polymerization – increases.

As the molecular weight, or degree of polymerization, increases, there is a sharp fall in the amount of cross-linking agent necessary for the formation of one cross link per polymer macromolecule, which is already sufficient for the conversion of the whole mass into one continuous macromolecule, i.e. for its conversion into a three-dimensional polymer. Fig. 3 shows the dependence of the amount of cross-linking agent necessary for the formation of one cross link per macromolecule on the degree of polymerization of the polymer that is being converted into a three-dimensional compound.

TABLE 2

Dependence of the Number of Cross Links per Polymer Macromolecule on the Degree of Polymerization of the Polymer and the Amount of Cross-linking Agent

x	y (moles per 100 basic moles of polymer)						
	100	50	10	5	1	0.1	0.01
1	1.0	0.5	0.1	0.05	0.01	0.001	0.0001
10	10.0	5.0	1.0	0.5	0.1	0.01	0.001
50	50.0	25.0	5.0	2.5	0.5	0.05	0.005
100	100.0	50.0	10.0	5.0	1.0	0.1	0.01
500	500.0	250.0	50.0	25.0	5.0	0.5	0.05
1,000	1000.0	500.0	100.0	50.0	10.0	1.0	0.1
10,000	10000.0	5000.0	1000.0	500.0	100.0	10.0	1.0

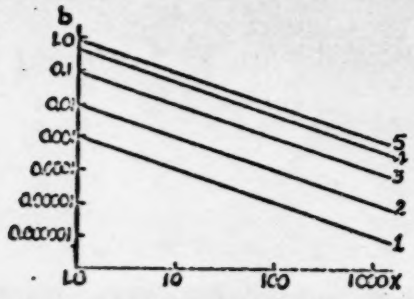


Fig. 1. Dependence of the number of cross links per repeating unit of polymer on the concentration of the cross-linking agent and on the molecular weight of the polymer: 1) $y' = 0.1$; 2) $y' = 1$; 3) $y' = 10$; 4) $y' = 50$; 5) $y' = 100$

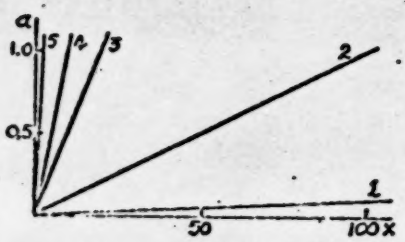


Fig. 2. Dependence of the number of cross links per macromolecule on the concentration of cross-linking agent and on the molecular weight of the polymer: 1) $y = 0.1$; 2) $y = 1$; 3) $y = 5$; 4) $y = 10$; 5) $y = 50$

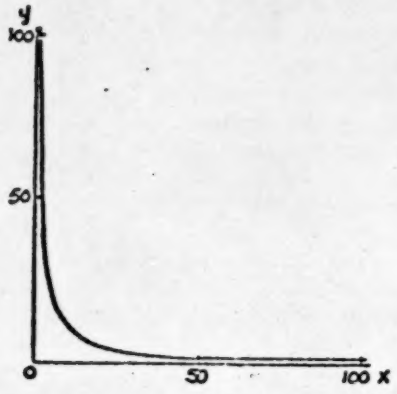


Fig. 3. Dependence of the concentration of cross-linking agent necessary for the formation of one cross link per macromolecule on the molecular weight of the polymer.

These considerations lead us to the conclusion that increase in the molecular weight of the polymer results in increased probability of reaction with cross-linking agent. Hence, when we have a mixture of molecules varying in size and subject it to the action of the cross-linking agent, the longer molecules are the first molecules to react. The molecules that react become cross-linked together, and at a definite stage of the process they are converted into the three-dimensional polymer. When the reaction conditions are such that the amount of cross-linking agent is insufficient to bring all of the molecules into the reaction and convert them into the three-dimensional polymer, the part of the linear polymer that does not react will include the shorter molecules. This conclusion, which has been derived theoretically, has been fully confirmed experimentally, as can be seen from the above-described results of the investigation of the reaction of poly-[ethylenephenyl] with dihalo compounds.

It is interesting to note the analogy that exists between the behavior of macromolecules of varying length in the cross-linking reaction discussed above and in degradation reactions, in which the longer molecules have been found in a number of cases to be more prone to attack. Thus, two of the present authors, in a study of the degradation of poly-[ethylenephenyl], have shown that degradation by means of benzene affects the longer molecules first [5]. One of us, in collaboration with Zamyatina [6], has made a similar observation for the degradation of polyamides with adipic acid or 1,6-hexanediamine. Similiar results were obtained also by one of the present authors, in collaboration with Golubev [7] and with Vinogradova [8], in a study of the degradation of polyesters by adipic acid or hexadecyl alcohol.

The theoretical basis of this peculiar feature of the chemical degradation of macromolecular compounds, treated on statistical principles, has been given by one of the present authors [9-14].

EXPERIMENTAL

The reactions between poly[ethylenephenyl] and dihalo compounds were carried out as follows. The polymer (5 g of a mixture of about 40% of poly[ethylenephenyl] of molecular weight 11,470 and 60% of poly-[ethylenephenyl] of molecular weight 2,140) was placed in a test tube, weighed amounts of the dihaloalkane and aluminum chloride were added, and the tube was closed with a stopper carrying a calcium chloride tube. The tube was then placed in a bath of Wood's metal and maintained at 120° with the aid of a contact thermometer and a relay.

TABLE 3

Experimental Conditions and Results for the Reaction of Poly[ethylenephenyl] with Dihaloalkanes

Dihaloalkane	Amount of dihaloalkane (g)	Amount of aluminum chloride (g)	Amount isolated after reaction, (g)		Properties of soluble poly-[ethylenephenyl]	
			of soluble poly-[ethylenephenyl]	of insoluble poly[ethyl-enephenyl]	Specific viscosity of a 3% solution in benzene	Molecular weight
Dibromomethane	0.18	0.12	4.172	0.882	0.327	6290
	0.54	0.38	4.132	0.765	0.266	5120
	0.72	0.50	4.025	1.001	0.162	3120
1,2-Dibromoethane	0.19	0.12	3.862	0.791	0.292	5610
	0.39	0.25	3.401	1.235	0.296	5700
	0.78	0.50	3.270	1.292	0.290	5580
	1.17	0.75	3.092	1.790	0.116	2230
1-Bromo-3-chloro propane	0.16	0.12	4.062	0.940	0.281	5400
	0.32	0.25	4.001	0.835	0.269	5170
	0.96	0.75	3.820	0.992	0.162	3110
1,4-Dibromobutane	0.22	0.12	4.230	0.245	0.318	6100
	0.68	0.38	3.965	0.335	0.289	5560
	0.90	0.50	3.572	0.492	0.268	5150
	1.35	0.75	4.081	0.720	0.230	4420
1,6-Dibromohexane	0.25	0.12	4.512	0.292	0.302	5810
	0.50	0.25	4.070	0.610	0.266	5110
	1.00	0.50	3.955	1.321	0.243	4670
	1.50	0.75	3.651	0.819	0.214	4110

Heating of the reaction mixture was continued for three hours, and dilute hydrochloric acid and benzene were then added to the contents of the test tube. The liquid was poured into a flask, and the remainder of the contents of the tube were quantitatively transferred to the flask, with the aid of benzene as solvent. The mixture, which consisted of a benzene solution of poly[ethylenephenyl], an aqueous layer, and insoluble three-dimensional polymer, was filtered through a weighed sintered-base glass crucible, and the residue on the filter was washed with benzene until the benzene was no longer colored. The crucible and contents were dried to constant weight at 150-170°, and from its weight the amount of insoluble polymer was determined.

The benzene layer of the filtrate was separated in a separating funnel, washed with water until neutral, and dried with calcium chloride. The calcium chloride was filtered off and washed with dry benzene, the washings being added to the main filtrate. The greater part of the benzene was distilled off, and the residue was freed from benzene by heating it at 150-170° until a constant weight was attained.

The amounts of materials taken for reaction and the experimental results are given in Table 3.

SUMMARY

1. A study has been made of reactions, resulting in the formation of products of three-dimensional structure, which occur when poly[ethylenephenyl] is treated with various dihaloalkanes in presence of anhydrous aluminum

chloride.

2. It has been shown experimentally that, in the formation of three-dimensional products from an artificially prepared mixture of poly[ethylenephenyl] preparations differing in molecular weight, the three-dimensional polymer is built up mainly from the polymer components of higher molecular weight.

3. It has been shown that, in the conversion of a linear polymer into a three-dimensional polymer, the probability of a macromolecule becoming cross-linked increases as its molecular weight increases.

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MACROMOLECULAR COMPOUNDS

COMMUNICATION 73. SOME TWO-COMPONENT MIXED POLYAMIDES

V. V. Korshak and T. M. Frunze

In a previous communication we have described mixed polyamides formed from 1,6-hexanediamine salts of two of the following acids: succinic, adipic, suberic, azelaic, and sebacic [1].

In vestigation showed that there is a definite relationship between the properties of a mixed polyamide obtained in this way and the proportions of the reactants. Mixed polyamides have lower melting points than either of the polyamides obtained from the single component salts. For each of the investigated series of polyamides, the minimum melting point corresponds to the polymer containing 60 mole-% of the acid having the higher number of methylene groups. It was found also that there is a linear relationship between the melting points of polyamides and the content of amide linkages in the macromolecular chain. This relationship enabled us to calculate the proportion of amide groupings that are unable, for purely stereochemical reasons, to form hydrogen bonds, it being to the existence of such groupings that we must attribute the lower melting points, and higher solubilities in organic solvents of mixed polyamides, as compared with straight polyamides prepared from one salt.

It would be very interesting to determine the extent to which these relationships remain valid when one of the salts is replaced by an amino acid. With this object we have investigated series of mixed polyamides derived from 6-caprolactam (2-oxohexamethylenimine) and 1,6-hexanediamine salts of adipic, azelaic, and sebacic acids. Of these series, that derived from 1,6-hexanediamine adipate and 6-caprolactam has been investigated by Catlin, Czerwin, and Willey [2], and the melting point curve that we have obtained for this series is in accord with that given by these investigators.

EXPERIMENTAL

The reactions were carried out by the procedure described previously [1]. The mixture of reactants was heated in test tubes for six hours in an atmosphere of nitrogen carefully purified from oxygen in the temperature range 200-250° (30 minutes at 200°, 30 minutes at 220°, and five hours at 250°).

Starting Materials.

The original dicarboxylic acids were purified by recrystallizing them at least twice from water. In the first recrystallizations of azelaic and sebacic acids, a little potassium permanganate was added to oxidize oily impurities. The degree of purity of the acids was checked by titration to phenolphthalein with 0.02 N NaOH. The melting points of the acids used in the experiments were: adipic 152.5° (reported value 153° [3]), azelaic 106° (reported value 106.5° [4]), and sebacic 134° (reported value 134.5° [5]).

1,6-Hexanediamine was purified by two distillations under a reduced pressure of nitrogen; 5-10% of caustic soda or 5% of sodium was added to the diamine — this addition increases the loss of diamine, but a purer product is obtained. The distillate of liquid diamine was collected in a receiver cooled with a mixture of snow and salt; rapid cooling and solidification of the diamine makes it possible to obtain a much purer product that that obtained when the diamine remains for some considerable time in the molten state. The diamine obtained in this way can be preserved for a long time unchanged. It melted at 42° and boiled at 100° (20 mm) (the reported melting point is 42° [6]). The 6-caprolactam was purified by distillation, and it then melted at 68° (the reported melting point is 68-70° [7]).

One of the present authors has shown, in collaboration with Rafikov [8] and Golubev [9], that the molecular weight of a polyamide obtained by the polycondensation of a diamine with a dicarboxylic acid is reduced greatly when an excess of diamine or dicarboxylic acid is present. Polyamides of the highest molecular weights, therefore, may be prepared only when strictly equivalent amounts of diamine and dicarboxylic acid are used. The simplest and most reliable method of ensuring that the reactants are applied in equimolecular proportions is the use of previously prepared neutral salts, for all dicarboxylic acids, apart from oxalic, readily form neutral salts with 1,6-hexanediamine [10].

For the preparation of the salts a weighed amount of the acid was dissolved in hot 80% ethanol. A 5% excess of 1,6-hexanediamine – molten or, better, as a solution in 80% ethanol – was carefully added to the resulting hot solution (with stirring to avoid boiling over), and the boiling solution of the salt was rapidly filtered through a glass filter and allowed to cool. The salt that crystallized out was filtered off at the pump and recrystallized from 80% ethanol. The crystals were filtered off and rapidly washed on the filter with 96% ethanol; they were then drained under suction as efficiently as possible, and dried in the air. Rapid washing is essential, for if it is prolonged, diamine is extracted and an acid salt is obtained. Also, it is essential to drain the salt as thoroughly as possible to remove alcohol used for washing, for if alcohol remains in the salt, the latter is oxidized during drying in the air. Alcoholic solutions of the salts also oxidize very readily, and it is not recommended that they be left overnight. The total amount of solvent used in the preparation of the salts is 500 ml for 200 g of the original acid and 500 ml for 300 g of crude salt in the second crystallization.

When the alcohol used is more dilute, more of the salt is lost, for it is more soluble in water than in alcohol. When 95% ethanol is used, the salt obtained is yellowish, probably owing to the greater ease with which such solutions undergo oxidation in the air. The excess of free acid in the salts was determined by titration to phenolphthalein with 0.02 N NaOH. The salt used must be neutral.

The salts used for the reactions were: 1,6-hexanediamine adipate (AdH), m.p. 190.8-191°, 1,6-hexanediamine sebacate (SH), m.p. 174°, and 1,6-hexanediamine azelaate (AzH), containing two molecules of water of crystallization and melting at 102° in a sealed capillary. Anhydrous 1,6-hexanediamine azelaate, m.p. 148°, can also be prepared.

RESULTS

The mixed polamides that we prepared contained residues of 6-aminohexanoic acid, 1,6-hexanediamine, and one of the following dicarboxylic acids: adipic, azelaic, and sebacic. The proportions of these residues varied according to the proportions of the substances taken for the preparation of the samples. The melting points of the products were determined by the method described previously [1], and their solubilities in alcohol and other solvents were measured. The viscosities of 0.5% solutions of the products in cresol were determined; the mean molecular weight of the products was about 15,000. The results obtained are given in the table.

TABLE

Melting Points of Mixed Polyamides

Molar ratio of starting materials**	Original substances*		
	AdH / C	AzH / C	SH / C
1/0	250-252	205-208	210-212
0.8/0.2	220-225	180-187	195-200
0.6/0.4	190-196	155-160	178-185
0.5/0.5	180-190	135-140	170-174
0.4/0.6	170-177	130-135	160-165
0.2/0.8	165-173	135-140	153-158
0.1/0.9	174-177	175-178	160-168
0/1	215-217	215-217	215-217

* Abbreviations: Ad - adipic acid; Az - azelaic acid; S - sebacic acid; H - 1,6-hexanediamine; C - 6-caprolactam

** The numerator and denominator of each ratio refer to the substances in the numerator and denominator respectively at the top of each column under the heading "Original substances".

DISCUSSION OF RESULTS

Figures 1, 2, and 3 show the variation in melting point with composition in the binary polymer systems studied.

These figures show that variation in the composition of the polymers is accompanied by variation in melting point and other properties. The melting points of mixed polyamides are lower than those of polyamides obtained from one component only. As the amount of the second component increases, the melting point falls and passes through a minimum corresponding to a product containing 6-caprolactam at a mole fraction of 0.8. It is interesting to note that this corresponds to about 60% by weight of caprolactam in the product, i.e. approximately the same proportion as we found for mixed polyamides obtained from salts of two dicarboxylic acids, for which the minimum melting point again corresponds to the product containing about 60% by weight of one of the components in its molecule [1].

For every series of polymers studied the minimum melting point is different, the lowest being found to be 130° for the AzH-C series, whereas for the AdH-C series it is 165°, and for the SH-C series it is 153°. Comparison of the series based on adipic and sebacic acids indicates that increase in the chain length of the dicarboxylic acid results in a lowering of the minimum melting point, but there are anomalies when the acid has an odd number of carbon atoms in its molecule, as can be seen from the behavior of the azelaic series, which has the lowest minimum melting point. As we have already shown [1], this can be explained by the reduced possibility of hydrogen-bond formation in polyamides derived from odd acids.

All of the polyamides that we have prepared are readily soluble in cresol, and many of them are dissolved when heated with ethanol or 2-methoxyethanol – with some difficulty, also 2-ethoxyethanol – but when cooled, these solu-

tions immediately gelatinize. None of them is soluble in cyclohexanone, chloroform, or benzene. The most soluble products are those of the AzH-C series, and this series is followed by SH-C and AdH-C. Within each series, the product of lowest melting point has the highest solubility.

Fig. 1.

Fig. 2.

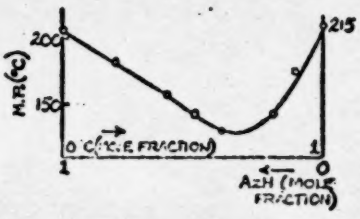

Fig. 3.

The variations in the properties of the investigated polyamides can be explained on the basis of the possibility of the formation of a greater or lower number of hydrogen bonds. A polyamide can be regarded as a polyethylene system in which, in addition to methylene groups, there are amide groupings, which, by forming hydrogen bonds, cause a raising of melting point and increase in mechanical strength which are directly proportional, to a first approximation, to the proportion of hydrogen bonds [1].

In mixed polyamides, not all of the amide groupings are able to form strong hydrogen bonds, owing to the operation of purely steric factors, which make it impossible for approaches to a distance of about 2.7 A to be made. For this reason, the presence of a certain number of amide groupings will affect the properties of a polyamide only to the extent to which these amide groupings can form hydrogen bonds with similar groupings in neighboring polyamide molecules. It may be noted in passing that, according to Mikhailov's results [11], the formation of intramolecular hydrogen bonds does not affect the melting point, but reduces the mechanical strength.

As will be seen from the scheme given below, in the mixed polyamide derived from the salt AdH and caprolactam taken in the proportions of 2 : 3, not all amide groupings are able to form hydrogen bonds:

```
-C-Ad-H-C-Ad-H-C-
-C-C-Ad-H-C-Ad-H-
-C-C-C-Ad-H-Ad-H-
```

If we represent the hydrogen bonds between amide groupings by dotted lines and indicate the number of atoms in each residue in the main chain of the mixed polyamide, we obtain the following picture:

```
-7-6-8-7-6-8-7-
  :     :     :
  :     :     :
-7-7-6-8-7-6-8-
  :           : : :
  :           : : :
-7-7-7-6-8-6-8-
```

It will be seen from this scheme that a considerable proportion of the amide groupings cannot form hydrogen bonds with amide groupings in neighboring molecules. This is the cause of the depressed melting points and enhanced solubilities of mixed polyamides.

For comparison, we give schemes for the formation of hydrogen bonds between amide groupings in straight polyamides, namely, the polyamide derived from the salt AdH (I) and that derived from caprolactam (II):

```
-C-8-6-8-6-8-6-8-
: : : : : : : : :
: : : : : : : : :
-6-8-6-8-6-8-6-8-
: : : : : : : : :
: : : : : : : : :
-6-8-6-8-6-8-6-8-
```

(I)

```
-7-7-7-7-7-7-7-7-
:   :   :   :   :
:   :   :   :   :
-7-7-7-7-7-7-7-7-
:   :   :   :   :
:   :   :   :   :
-7-7-7-7-7-7-7-7-
```

(II)

It can be readily seen that in straight polyamides the number of hydrogen bonds formed between the macromole-

cule chains will be very much greater than in mixed polyamides. It is interesting to note the great difference in the number of hydrogen bonds between the straight polymers derived from the salt AdH and from caprolactam; here, evidently, lies the cause of the considerable difference in melting point between poly[1,6-hexanediamine adipate] (I, m.p. 250°) and polycaprolactam (II, m.p. 215°).

Reaction Mechanism for the Formation of Mixed Polyamides

When mixed polyamides containing residues of 6-aminohexanoic acid are prepared with the aid of the lactam of 6-aminohexanoic acid caprolactam as one of the components, the reaction is a very complex process, and includes simultaneous polymerization and polycondensation reactions. The contribution made to the process by each of these types of reactions varies greatly at various stages of the process: it varies with time, and it depends to a lesser extent on the original composition of the reaction mixture. In the initial stage of the reaction, polymerization of 6-caprolactam and polycondensation of the second component, the salt of 1,6-hexanediamine with a dicarboxylic acid, proceed simultaneously. However, as the process proceeds, the part played by the polymerization reaction becomes less and less significant, owing to the exhaustion of the caprolactam, whereas the role of the polycondensation reaction becomes more and more important, and is ultimately predominant.

It is known [12] that the polymerization of 6-caprolactam proceeds in presence of water [13], acids [14], amines, alcohols, and other substances containing mobile hydrogen atoms [15] and is a special case of "hydrolytic" polymerization, the term proposed for the polymerization of cyclic lactams, cyclic esters, aldehydes, ketones, and other compounds of this type [16-18], as distinct from the polymerization of unsaturated compounds, which proceeds, according to the structure of the monomer and the mode of initiation, as "radical" or as "ionic" polymerization [19].

An example of hydrolytic polymerization is the polymerization of 6-caprolactam, which, in the processes dealt with in this paper, occurs in presence of an activator, namely, the 1,6-hexanediamine dicarboxylic acid salt added as second component. Each of the components forming the salt is capable of bringing about the polymerization of 6-caprolactam, chain growth being initiated according to the following scheme:

$$H_2N(CH_2)_6NH_2 + \underbrace{NH(CH_2)_5CO} \longrightarrow H_2N(CH_2)_6NHCO(CH_2)_5NH_2$$

$$HOOC(CH_2)_4COOH + \underbrace{NH(CH_2)_5CO} \longrightarrow HOOC(CH_2)_4CONH(CH_2)_5COOH$$

The resulting addition compound formed between the activator and the 6-caprolactam molecule enters into reaction with further caprolactam molecules, with formation of a polymer molecule according to the scheme:

$$H_2N(CH_2)_6NHCO(CH_2)_5NH_2 + x\ \underbrace{NH(CH_2)_5CO} \longrightarrow H_2N(CH_2)_6NH[CO(CH_2)_5NH]_xH$$

$$HOOC(CH_2)_4CONH(CH_2)_5COOH + x\ \underbrace{NH(CH_2)_5CO} \longrightarrow HOOC(CH_2)_4CO[NH(CH_2)_5CO]_xOH$$

An interesting feature of the polymer so formed is the presence of terminal groupings consisting of residues of the activator used for the polymerization of the 6-caprolactam.

Also, water is formed in the polycondensation of the dicarboxylic acid salt of 1,6-hexanediamine, and in the first stage of the process this leads to the formation of 6-aminohexanoic acid, which reacts further in accordance with the above scheme, with formation of polycaprolactam:

$$H_2O + \underbrace{NH(CH_2)_5CO} \longrightarrow H_2N(CH_2)_5COOH$$

$$H_2N(CH_2)_5COOH + x\ \underbrace{NH(CH_2)_5CO} \longrightarrow H[HN(CH_2)_5CO]_{x+1}OH$$

However, the part played by water-initiated polymerization in the reactions we have investigated is evidently not great, for water vapor will be removed rapidly by the current of nitrogen passing through the reaction vessel.

The second component in the preparation of mixed polyamides (in our experiments this was the 1,6-hexanediamine salt of adipic, azelaic, or sebacic acid) can form a polymer only by a polycondensation reaction, which proceeds according to the equation:

$$xH_2N(CH_2)_6NH_2 + x\ HOOC(CH_2)_4COOH \longrightarrow H[NH(CH_2)_6NHCO(CH_2)_4CO]_xOH + (2x-1)\ H_2O.$$

One of the present authors, with Rafikov [20], has shown that a factor favoring the polycondensation of the salts of diamines with dicarboxylic acids is their linear structure. An investigation of 1,6-hexanediamine adipate has shown that it has a linear structure [20]. Other workers have also expressed a similar opinion about the structure of these salts [21-24]. Shpitalny, Mezos, and Koretskaya [25] have recently suggested the possibility of a cyclic structure for salts of diamines with dicarboxylic acids, but in the complete absence of any experimental support for this suggestion, it cannot be regarded as proved.

The main difference in principle between polymerization and polycondensation is that, in the first reaction, there is separation of a product of low molecular weight (water, alcohol, etc.), whereas in the second, no such product is formed; this difference is determined by the nature of the original reacting substances. The products of the polymerization of 6-caprolactam have certain peculiarities, in that they have functional groups – amino and carboxyl – at the ends of their macromolecules, and these are able to react with one another and with similar groups in other molecules.

At any stage of the process, therefore, polymers of 6-caprolactam are able to undergo polycondensation among themselves, with molecules of the 1,6-hexanediamine salt of the dicarboxylic acid, and with polyamides formed by the polycondensation of this salt. It is this polycondensation process, together with exchange reactions that we shall consider later, which is mainly responsible for the formation of a mixed polyamide, rather than a mixture of two polyamides, as the final product of the reaction.

One of the present authors, working with Bretler, Pavlova, and Finogenov [26], has made a detailed investigation of the mixed polyamide obtained by the polycondensation of a mixture of 20% of the salt SH, 40% of the salt AdH, and 40% of 6-caprolactam. Fractionation of this polyamide showed that it is a mixed polyamide, and not a mixture of various polyamides. Investigation of the molecular weight distribution function for this polyamide with the aid of the ultracentrifuge showed that this product was completely homogeneous.

The homogeneity in composition of mixed polyamides is determined also by the occurrence of exchange reactions, which result in a "leveling out" of the compositions of the macromolecules formed. Thus, in the same investigation [26] it was shown that heating of a mixture of two polyamide fractions differing in molecular weight resulted in the formation of a polyamide having an intermediate molecular weight corresponding to a state of polycondensation equilibrium under the given conditions. The great importance of exchange reactions in the polycondensation process, as a factor determining the leveling out of the compositions of the macromolecules formed, has been shown for a large number of other examples of the polycondensation reaction [27-29].

The tendency for polyamide macromolecules to react with one another with participation of the terminal amino and carboxyl groups must be fairly high, judging from the results of one of the present authors and Vinogradova [30] on the polycondensation of dicarboxylic acids with glycols, in which the main reaction leading to the formation of macromolecules polyesters was found to be the interaction between polyester molecules. The high reactivities of the macromolecules of polyurethanes was shown by one of us and Cherkova [31] in a study of the heteropolymerization of diisocyanates with glycols.

On the basis of these results it may be supposed that in polyamide formation the main way in which large macromolecules are formed is by the interaction of already formed polyamide macromolecules. Hence, in the formation of mixed polyamides, the last stage will be the polycondensation of polyamide macromolecules of various lengths with one another, and the very largest macromolecules, being much beyond the average size, will have the greatest tendency to undergo breakdown in degradative reactions, so that, in accord with actual observations [26], a polymer of low polydispersity will be formed.

SUMMARY

1. A study has been made of mixed binary polyamides formed from 6-caprolactam and a salt of 1,6-hexanediamine with adipic, azelaic, or sebacic acid.

2. It has been found that each of these series of polyamides has a minimum melting point when the mole percentage of 6-caprolactam is 80.

3. A reaction mechanism has been proposed for the formation of mixed polyamides from components that include 6-caprolactam.

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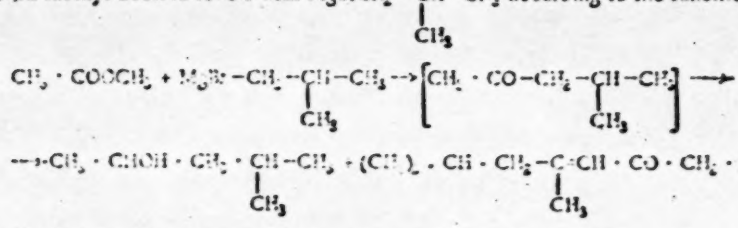
BRIEF COMMUNICATIONS

REACTION OF 2-METHYLALLYLMAGNESIUM CHLORIDE WITH ESTERS OF PALMITIC AND 2-ETHYLHEXANOIC ACIDS

A. D. Petrov, V. M. Melekhin, and A. M. Nefedov

In a series of investigations Petrov and coworkers [1] have shown that tert-alkylmagnesium halides (tert-butylmagnesium chloride) react with esters of monobasic aliphatic acids in accordance with the so-called "anomalous" scheme, with formation of ketones of the type R · CO · R, though acids of low molecular weight also give ketones of type R · CO · R' and their reduction products – the secondary alcohols R · CHOH · R'.

Isobutylmagnesium halides also react anomalously with esters of monobasic acids. As Shine and Turner showed [2], even methyl acetate reacts with $MgBrCH_2 \cdot CH(CH_3)-CH_3$ according to the scheme:



$$CH_3 \cdot COOCH_3 + MgBrCH_2-CH(CH_3)-CH_3 \rightarrow \left[CH_3 \cdot CO-CH_2-CH(CH_3)-CH_3\right] \rightarrow$$

$$\rightarrow CH_3 \cdot CHOH \cdot CH_2 \cdot CH(CH_3)-CH_3 + (CH_3)_2 \cdot CH \cdot CH_2-C(CH_3)=CH \cdot CO \cdot CH_2 \cdot CH(CH_3)_2$$

i.e., with formation of both the secondary alcohol R · CHOH · R' and the product of the dehydrational condensation of the ketone R · CO · R'.

Grignard reagents derived from compounds of the allyl halide type have already been widely studied in Grignard-Wurtz reactions, and the extensive material now available shows that their use in place of the corresponding saturated compounds commonly called stabilizes and considerably increases the yields of hydrocarbons of the desired structure [3]. However, the reactions of carbonyl compounds (ketones and esters) with allyl magnesium halides having a double bond in the β-position have received almost no study at all, though it may be predicted that these reagents will react mainly by the "normal" scheme with the formation of much smaller amounts of "anomalous" reaction products. The present work was carried out with the object of filling this gap. It has been established that methyl palmitate reacts with 2-methylallylmagnesium chloride initially according to the normal scheme, a 50% yield of 2-methyl-4-(2-methylallyl)-1-octadecen-4-ol being formed (the yield of palmitone (18-pentatriacontanone), formed by the anomalous scheme, was only 5%). When an ester of lower molecular weight – methyl 2-ethylhexanoate – was used, the corresponding tertiary alcohol was obtained in 69% yield, and no anomalous products were isolated. The alcohols obtained were hydrogenated to the saturated tertiary alcohols, the products were dehydrated to olefins, and the olefins were hydrogenated to paraffin hydrocarbons, namely, 4-isobutyl-2-methylundecane (freezing at -10° to a crystalline solid) and 5-ethyl-4-isobutyl-2-methylnonane (freezing to a glass at -90°).

EXPERIMENTAL

2-Methyl-4-(2-methylallyl)-1-octadecen-4-ol. In accordance with Yavorsky's method, a mixture of 453.5 g (1.68 moles) of methyl palmitate and 300 g (3.3 moles) of 2-methylallyl chloride dissolved in 1000 ml of ether was added, under stirring, to 105 g (4.41 moles) of magnesium in 500 ml of ether. After being heated for 36 hours, the mixture was decomposed, the ether layer was separated, and the ether was distilled off. The reaction products were separated by vacuum fractionation, and 165 g (0.61 mole) of unchanged methyl palmitate, boiling at 146-156° (3 mm) and melting at 30°, was obtained, and also 210 g of a fraction boiling at 230° (3 mm) (56% yield on the amount of methyl palmitate that reacted). This substance had n_D^{20} 1.4611; d_4^{20} 0.8582; Kaufmann bromine number 89.96 (calculated 91.27); OH content by the Tserevitinov reaction 5.01% (calculated for $C_{22}H_{44}O$ 4.86%). This tertiary alcohol readily gave a carbanilic ester (phenylurethan) in the cold; it melted at 89.5°.

$C_{29}H_{55}NO_2$. Found %: C 79.32; H 11.23
Calculated %: C 79.20; H 10.94

When the tertiary alcohol was distilled, a solid residue (7.8 g) remained in the flask, it melted at 62°.

Found %: C 82.08; H 13.83
$C_{21}H_{42}O$. Calculated %: C 82.50; H 13.86

Its oxime was prepared and was found to melt at 58.5°.

2-Isobutyl-2-methylnonadecane. 2-Methyl-4-(2-methylallyl)-1-nonadecen-4-ol (50 g) was dissolved in 150 ml of methanol and hydrogenated over Raney nickel in an autoclave, first at room temperature and 100 atm, and then at about 150°. After 20 hours the autoclave was cooled and the methanol was distilled off. 2-Isobutyl-2-methyl-4-nonadecanol was found to have the following properties: b.p. 197° (2 mm), n_D^{20} 1.4515; d_4^{20} 0.8413.

Landa [4] has dehydrated similar tertiary alcohols (3-ethyl-3-octadecanol and others) by heating them with zinc chloride at about 120°. Examination of the oxidation products of the resulting substances showed that dehydration occurred preferentially in the smallest of the radicals at the tertiary carbon. No isomeric changes were observed. Nevertheless, we attempted to effect the dehydration by Pschinbetzom's method [5], namely, heating at 150° with acetic anhydride and sodium acetate. However, even when heating was prolonged for 60 hours, less than one-third of the compound had undergone dehydration, i.e. the method appeared to be unsuitable for alcohols of high molecular weight.

We then decided to prepare the olefin by pyrolysis, not of the acetic ester of the alcohol, but of its ester with an acid of higher molecular weight, namely, 2-ethylhexanoic acid. It was found, however, that already in the process of preparing this ester, the olefin was formed, and was obtained instead of the ester. A mixture of 12.2 g of 4-isobutyl-2-methyl-4-nonadecanol, 11 g of 2-ethylhexanoic acid (boiling at 116-118° at 13 mm), and 1 ml of sulfuric acid was refluxed for seven hours. Vacuum fractionation of the reaction products yielded a fraction of b.p. 191-192° (4 mm), n_D^{20} 1.4526, d_4^{20} 0.8033, found MR 113.17; calculated MR 112.57.

Found %: C 85.26, H 14.79
$C_{25}H_{50}$. Calculated %: C 85.63, H 14.37

Hydrogenation of this olefin fraction was carried out over Raney nickel for nine hours at 130°, the initial pressure of hydrogen being 145 atm. The hydrogenation product boiled at 192-193° at 3 mm and froze to a crystalline substance at -10°; it had n_D^{20} 1.4510; d_4^{20} 0.8013, found MR 113.76; calculated MR 113.03.

Found %: C 85.45, H 14.62
$C_{25}H_{52}$. Calculated %: C 85.12; H 14.88

5-Ethyl-2-methyl-4-(2-methylallyl)-1-octen-4-ol. 2-Ethylhexanoic acid (b.p. 116-118° (13 mm), n_D^{20} 1.4260, d_4^{20} 0.9172) was converted into its methyl ester (b.p. 94-97° (14.5 mm), n_D^{20} 1.4162; d_4^{20} 0.8731). In accordance with Yatsenko's method, a mixture of 45 g of methyl 2-ethylhexanoate and 111 g of 2-methylallyl chloride dissolved in 300 ml of ether was added to 50 g of magnesium in 200 ml of ether. The mixture was heated for ten hours, and decomposition was then effected with water and ammonium chloride. An 80% yield of 5-ethyl-2-methyl-4-(2-methylallyl)-1-octen-4-ol was obtained, b.p. 131-132° (10 mm), n_D^{20} 1.4669; d_4^{20} 0.8974, found MR 76.12, calculated MR 76.65.

Found %: C 80.30; H 12.41
$C_{14}H_{26}O$. Calculated %: C 80.69; H 12.63

The alcohol was hydrogenated under the same conditions as those used for the above-described diolefinic alcohol. The product was an alcohol of composition $C_{14}H_{30}O$, b.p. 124-125° (10 mm), n_D^{20} 1.4468; d_4^{20} 0.8336, found MR 77.61, calculated MR 77.14.

Found %: C 79.23, H 14.09
$C_{14}H_{30}O$. Calculated %: C 79.26; H 14.14

5-Ethyl-4-isobutyl-2-methylnonane. Dehydration of 10 g of the alcohol $C_{14}H_{30}O$ was effected by Landa's method [4], the alcohol being heated for three hours at 190° with 1.5 g of anhydrous zinc chloride. A mixture of olefins of composition $C_{14}H_{28}$ was obtained; they had b.p. 120° (10 mm); n_D^{20} 1.4429; d_4^{20} 0.7853; found MR 75.70; calculated MR 75.62.

Hydrogenation under the conditions given above yielded a paraffin hydrocarbon boiling at 108-109° at 10 mm and freezing at -60°. It had n_D^{20} 1.4421; d_4^{20} 0.7936.

Found %: C 85.19, H 14.95
$C_{14}H_{30}$. Calculated %: C 84.85; H 15.14

SUMMARY

1. It has been shown that the reaction of methyl palmitate with 2-methylallylmagnesium chloride proceeds mainly according to the normal scheme, 2-methyl-2-(2-methylallyl)-1-nonadecen-4-ol being obtained in 56% yield. The yield of palmitone (16-hentriacontanone), formed by the anomalous reaction, was only 8%.

2. When the reaction was carried out with the methyl ester of an acid of lower molecular weight but of branched structure – 2-ethylhexanoic acid – the yield of the corresponding tertiary alcohol was as high as 87%, and no anomalous products were formed.

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